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BUFFER ADDITIVES FOR LIME/LIMESTONE SLURRY SCRUBBING SYNTHESIS, MASS TRANSFER, AND DEGRADATION

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FOR
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SYNTHESIS, MASS TRANSFER, AND DEGRADATION

by

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16. ABSTRACT The report gives results of experimental studies, performed with buffer additives, useful for flue gas desulfurization by lime/limestone slurry scrubbing. Rates of reaction of acrylic acid and maleic anhydride with bisulfite at 55 C were sufficiently fast to permit in situ synthesis in a slurry scrubber of sulfopropionic and sulfosuccinic acids, respectively. Beta-hydroxypropionic acid was synthesized by hydration of acrylic acid at 100-140 C with catalysis by H2SO4 or cation exchange resin. Enhancement of SO2 absorption by acetic, adipic, hydroxypropionic, sulfopropionic, and sulfosuccinic acids and by basic aluminum sulfate was measured at 55 C in 0.3 M NaCl and 0.1 M CaCl2, and was successfully modeled by mass transfer with equilibrium reactions. Oxidation of carboxylic acids conjugated with oxidation of CaSO3 slurry was studied for seven acids. Oxidative degradation of adipic acid and other aliphatic and sulfocarboxylic acids was least at pH 4.3 with 1.0 mM dissolved Mn, and greatest at pH 5.5 without Mn. Hydroxyacetic and hydroxypropionic acids inhibited sulfite oxidation and were less subject to degradation. The most attractive acids for further testing are adipic, mixtures of waste dibasic organic, sulfosuccinic, hydroxypropionic, and hydroxyacetic acids.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
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Buffers (Chemistry)		Stationary Sources	07D	
Additives	Slurries		11G	
Flue Gases	Synthesis		21B	14G
Desulfurization	Mass Transfer		07A	
Scrubbers	Degradation		13I	
Calcium Oxides	Organic Acids		07B	07C

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ABSTRACT

Experimental studies were performed with buffer additives useful for flue gas desulfurization by lime/limestone slurry scrubbing. The rates of reaction of acrylic acid and maleic anhydride with bisulfite at 55°C were sufficiently fast to permit *in situ* synthesis in a slurry scrubber of sulfopropionic and sulfosuccinic acid, respectively. β-Hydroxypropionic acid was synthesized by hydration of acrylic acid at 100 to 140°C with catalysis by H_2SO_4 or cation exchange resin. Enhancement of SO_2 absorption by acetic, adipic, hydroxypropionic, sulfopropionic, and sulfosuccinic acids and by basic aluminum sulfate was measured at 55°C in 0.3 M NaCl and 0.1 M $CaCl_2$ and was successfully modeled by mass transfer with equilibrium reactions. Oxidation of carboxylic acids conjugated with oxidation of $CaSO_3$ slurry was studied for seven acids. Oxidative degradation of adipic acid and other aliphatic and sulfocarboxylic acids was least at pH 4.3 with 1.0 mM dissolved Mn and greatest at pH 5.5 without Mn. Hydroxyacetic and hydroxypropionic acids inhibited sulfite oxidation and were less subject to degradation. The most attractive acids for further testing are adipic, mixtures of waste dibasic organic acids, sulfosuccinic, hydroxypropionic, and hydroxyacetic.

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PROJECT SUMMARY

INTRODUCTION

Lime/limestone slurry scrubbing is the dominant commercial technology for flue gas desulfurization (Laseke et al., 1983). SO_2 is absorbed at 50-55°C and pH 4.5-6.0 in an aqueous slurry of excess limestone and product solids (Rochelle and King, 1978). The calcium sulfite ($CaSO_3$)/calcium sulfate ($CaSO_4$) product is disposed of as solid waste. With greater than 500-1000 ppm SO_2 in the flue gas, SO_2 absorption is controlled by liquid-film mass transfer resistance because of the limited solubility of SO_2 gas and alkaline solids. Additives that buffer between pH 3 and pH 5.5 enhance SO_2 absorption by providing dissolved alkaline species for reaction with SO_2 (Rochelle and King, 1977). This is a report of experimental investigations to provide data for the evaluation of buffer additive alternatives. This work has been summarized previously (Rochelle et al., 1982) and has been included in an extensive review of buffer additives (Rochelle, 1982).

An attractive buffer additive should be inexpensive, should provide mass transfer enhancement at low concentrations, and should be nonvolatile and chemically stable at scrubber conditions. The important classes of inexpensive, nonvolatile buffers include polycarboxylic acids such as adipic, hydroxycarboxylic acids such as hydroxypropionic, and sulfocarboxylic acids such as sulfopropionic. Some of these alternatives are not commercially available and must be synthesized from inexpensive raw materials. Cavanaugh (1978) demonstrated the synthesis of hydroxypropionic, sulfopropionic, and sulfosuccinic acids. This report presents quantitative reaction kinetics for the synthesis of these three alternatives. This work has also been published as a master's thesis by Smith (1981).

Mass transfer enhancement depends on the buffering properties and diffusivity of the additive. Cavanaugh (1978) measured effective pk_a values of buffer alternatives at scrubber conditions. Chang and Rochelle (1981) developed a model of enhancement based on mass transfer with equilibrium reactions and experimentally demonstrated its effectiveness with acetic and adipic acid at 25°C. This report presents experimental and model results at 55°C with several buffer alternatives. Details of the work are also given in a master's thesis by Weems (1981).

Organic acids are normally stable to oxidation, but laboratory and pilot plant results (Meserole et al., 1979) have shown that adipic acid oxidizes in conjugation with sulfite oxidation in the scrubber. This report gives oxidative degradation rates of adipic acid as a function of pH and Mn concentration. Results are also presented on glutaric, succinic, sulfopropionic, sulfosuccinic, fumaric, hydroxypropionic, and hydroxyacetic acids. Details of the work are given in master's theses by Hsiang (1981) and Garcia (1980).

BUFFER SYNTHESIS

Sulfocarboxylic and hydroxycarboxylic acids are attractive as buffer additives because the additional hydrophilic groups make both the buffer and its degradation products nonvolatile in aqueous solution. Rochelle (1977) evaluated available kinetic data on sulfite addition to maleic or acrylic acid to give sulfosuccinic or β-sulfopropionic acid. Cavanaugh (1978) demonstrated the feasibility of hydrating acrylic acid with H_2SO_4 catalysis at 100°C to get β-hydroxypropionic acid.

This report gives measurements of reaction kinetics for sulfonation of maleic, fumaric, and acrylic acids by sulfite addition and for hydration of acrylic acid with catalysis by H_2SO_4 or cation exchange resin. The kinetics were measured by sampling of isothermal batch reactors.

Sulfocarboxylic Acids

In sulfonation experiments the extent of reaction was determined by iodine titration for total sulfite. Solutions initially containing 0.05 to 0.20 M unsaturated acid were maintained at approximate pH values by lactate, acetate, or phosphate buffers. NaCl, $CaCl_2$, or $MgCl_2$ were added to give changes in ionic environment.

The sulfonation reactions follow a second-order mechanism:

$$\text{rate (M/min)} = k_f\,[\text{acid}]_{\text{Total}}\,[SO_3^{=}]_{\text{Total}}$$

The measured second-order rate constants, k_f ($M^{-1}\ min^{-1}$), for sulfonation at 1.2 N ionic strength in Na^+ solutions at pH 5 are given by:

acrylic: $k_f = 4.48 \times 10^8 \exp(-14{,}100/RT)$

fumaric: $k_f = 372 \exp(-6100/RT)$

maleic: $k_f = 2.38 \times 10^{11} \exp(-17{,}500/RT)$

where T is temperature (°K) and R is the gas constant (1.987 cal/gmol °K). At 55°C with 0.5 N ionic strength the constants are 0.21 $M^{-1}min^{-1}$ for acrylic, 0.031 $M^{-1}min^{-1}$ for fumaric, and 0.52 $M^{-1}min^{-1}$ for maleic.

The rate constants do not vary significantly from pH 3.5 to 7.0, but no reaction occurs at pH 2 or 13. The sulfonation rates increase with ionic strength. With fumaric and maleic acids, there may also be an additional catalytic effect of Mg^{++} or Ca^{++}.

Because dissolved sulfite is present in a typical $CaO/CaCO_3$ scrubber system, it is conceivable that unsaturated acids would sulfonate if added directly to the scrubber system. For the sulfonation reactions, a scrubber system can be characterized as a completely stirred tank reactor with a residence time equal to the ratio of solution inventory and the rate of loss of solution with the waste solids. Assuming 10 mM total dissolved sulfite, 55°C, 0.5 N ionic strength, and 130 hours residence time, the fraction of unsulfonated acid that would leave the system is 6% for acrylic, 29% for fumaric, and 4% for maleic. Therefore, *in situ* sulfonation is feasible for acrylic acid and maleic acid, but it is only partially effective for fumaric acid.

Acrylic acid and maleic anhydride (the commercial form of maleic acid) require some precautions for safe handling. If these precautions are unacceptable to the user, these unsaturated acids can be easily sulfonated offsite by reaction with sodium sulfite. Sodium sulfosuccinate was prepared successfully by adding 3.3 gmol Na_2SO_3 and 3.0 gmol maleic anhydride to one liter of water. The temperature increased from 25 to 80°C and the solids dissolved within one minute. The solution did not precipitate when cooled to 6°C. Therefore, the sulfonated acids could probably be prepared in a tank car and shipped as concentrated solution directly to the user.

Hydroxypropionic Acid (HP)

In hydration experiments, acrylic acid (AA) was determined by ion exclusion chromatography (ICE) on a Dionex ion chromatograph. Hydroxypropionic acid (HP) was evident on the chromatograms, but was not quantified because of the lack of an adequate standard. Hydration was catalyzed at 100 to 140°C by 0.1 to 1.5 M H_2SO_4 or by H^+-loaded sulfonated polystyrene resin (Dowex 50W-X4) with an exchange capacity of 1.3 meq/cm^3 (wet basis) and 67% moisture content.

The hydration reaction was found to be first-order in acrylic acid and first-order in H^+. The second order forward rate constant, k_f ($M^{-1}hr^{-1}$), for both resin and H_2SO_4 catalysis was correlated by:

$$k_f = 1.14 \times 10^9 \exp(-17{,}000/RT)$$

The reaction is reversible at high conversions, where the net reaction is given by:

$$\text{rate (M/hr)} = k_f[H^+]\,[AA] - k_f/K[H^+]\,[HP]$$

The equilibrium constant K is defined by:

$$K = [HP] / [AA]$$

Pressman and Lucas (1942) found K to be 11.3 at 110.6°C and 6.8 at 134°C.

In at least one experiment (105°C, 4 M AA, 0.5 M H_2SO_4), there was visual evidence of acrylic acid polymerization, giving a faster apparent rate constant. Polymerization should be minimized by reduced acrylic acid concentrations and increased catalyst concentrations.

Using the measured rate data and equilibria from Pressman and Lucas (1942), the estimated reactor residence times for 85% conversion with 1 M H_2SO_4 at 105°C are 14 hours for a batch or plug flow reactor, 85 hours for a single completely stirred tank reactor (CSTR), or 33 hours for two CSTR's in series. If the reaction was carried out at the scrubber site, no additional purification should be required, but there would be a makeup requirement for sulfuric acid.

Specific results with hydroxypropionic acid synthesized from acrylic acid indicate that it inhibits limestone dissolution (Chan and Rochelle, 1982). Inhibition probably results from polyacrylic acid formed during hydration. In actual operation, the polyacrylic acid may be removed from scrubber solution by precipitation of its calcium salt. If not, removal of polyacrylic acid by other means may be necessary.

GAS/LIQUID MASS TRANSFER ENHANCEMENT

Chang and Rochelle (1981) measured SO_2 absorption at 25°C in a continuous stirred reactor with an unbroken gas/liquid interface. They varied P_{SO_2}, pH, and concentrations of acetic acid and adipic acid in 0.3 M NaCl. Because SO_2 absorption was quantified by liquid-phase material balance, there were no experiments with greater than 1 mM total dissolved sulfite.

The apparatus used by Chang and Rochelle was modified for this work (Weems, 1981). Heating tape was added to liquid and gas stream inlets to permit operation at 55°C. Gas phase analysis and flow measurement were refined, and SO_2 absorption rate was determined by gas-phase material balance, permitting operation with high concentrations of sulfate and total sulfite. Tighter pH control was achieved by continuously adding 1.0 M NaOH directly to the reactor.

The apparatus was characterized at 55°C and 540 rpm by SO_2 absorption into 0.3 M NaOH giving a gas-film mass transfer coefficient ($k_g A$) of 4.93×10^{-3} gmol/bar-sec and into 0.3 MHCl giving a liquid-film mass transfer coefficient ($k^o_\ell A$) of 1.5×10^{-3} 1/sec, where A is the apparent surface area for mass transfer. Experiments were performed in 0.3 M NaCl or 0.1 M $CaCl_2$ at pH 5.5 or 4.2 with 0 to 40 mM of adipic, acetic, sulfopropionic, sulfosuccinic, or hydroxypropionic acids or $AlCl_3$. The gas-phase SO_2 concentration was adjusted to give about 1000 ppm at the gas-liquid interface. The enhancement of the liquid-film mass transfer coefficient by chemical reaction was calculated from SO_2 absorption rate, SO_2 gas concentration, SO_2 Henry's constant, $k^o_\ell A$, and $k_g A$ as in Chang and Rochelle (1981).

Chang and Rochelle (1981) developed an enhancement factor model based on approximate surface renewal with multiple equilibrium reactions. Their model included equilibria among and diffusion of the solution species: H^+, SO_2, HSO_3^-, $SO_3^=$, H_2A, HA^-, and $A^=$. The pk_a values of the buffer species, H_2A, HA^-, and $A^=$, could be adjusted to represent any appropriate buffer.

The model of Chang and Rochelle (1981) was used in this work with appropriate equilibrium constants and diffusivities to represent operation at 55°C in 0.3 M NaCl or 0.1 M $CaCl_2$ (Tables 3 and 4). Empirically, it was found that diffusivities in 0.1 M $CaCl_2$ were consistently less than in 0.3 M NaCl. To get good correlation of the experimental data the diffusivities of all monovalent anions were reduced 25% and the diffusivities of all divalent anions were reduced 45% from their values in 0.3 NaCl.

The calculated values of the liquid-film enhancement factor are within 10% of the measured values for adipic, acetic, sulfosuccinic, and hydroxypropionic acids. In order to fit the measured data, the diffusivity of sulfopropionic acid was reduced by an additional 50% from the value estimated by Chang and Rochelle (1981).

Experiments with up to 20 mM $AlCl_3$ in 0.1 M $CaCl_2$ at pH 3.8 gave no measureable enhancement of SO_2 absorption, even though basic aluminum chloride is an excellent buffer at pH 3.8. The lack of effectiveness of the aluminum buffer may result from the formation of large, slow-moving polynuclear aluminum complexes, or it may reflect a slow reaction rate between aluminum complexes and H^+.

Figure 1 shows the calculated liquid-film enhancement factor for five buffers as a function of buffer concentration in 0.1 M $CaCl_2$ at pH 5.5 with 1000 ppm SO_2 at the gas/liquid interface. On a molarity basis, adipic acid is most attractive and sulfopropionic acid is least attractive. With no buffer, the enhancement factor is 7.3 because of the hydrolysis of SO_2 and because of enhancement by $SO_3^=$. At 10 mM total adipic acid, the enhancement factor is 20, or about 3 times greater than in the absence of buffer.

Figure 2 illustrates the effect of adipic acid on the overall enhancement of SO_2 absorption. It gives the ratio of the overall mass transfer coefficient, K_g, to the gas film coefficient, k_g, as a function of the dimensionless liquid phase driving force, $(HP_{SO_2} + [HA\ ] + 2[A\ ])/HP_{SO_2}$, where H is the Henry's constant, P_{SO_2} is the bulk gas SO_2 partial pressure, and HA^- and $A^=$ represent H adipate and adipate species. The overall coefficient includes an effect of k_ℓ^o and the liquid-film enhancement factor which increases with adipic acid concentration. The ratio, K_g/k_g, represents the fraction resistance of the gas film and cannot exceed 1.0.

Greater values of K_g/k_g represent proportionately better scrubber performance. This specific figure is valid for scrubbers with the ratio of mass transfer coefficients without enhancement given by $H\,k_\ell^o/k_g$ equal to 0.2.

As shown in Figure 2, adipic acid will have a greater effect with higher SO_2 gas concentration, because at lower concentration SO_2 absorption is already controlled mostly by gas film resistance. With less total dissolved sulfite, liquid-film resistance is reduced by SO_2 hydrolysis to H^+ and HSO_3^-,

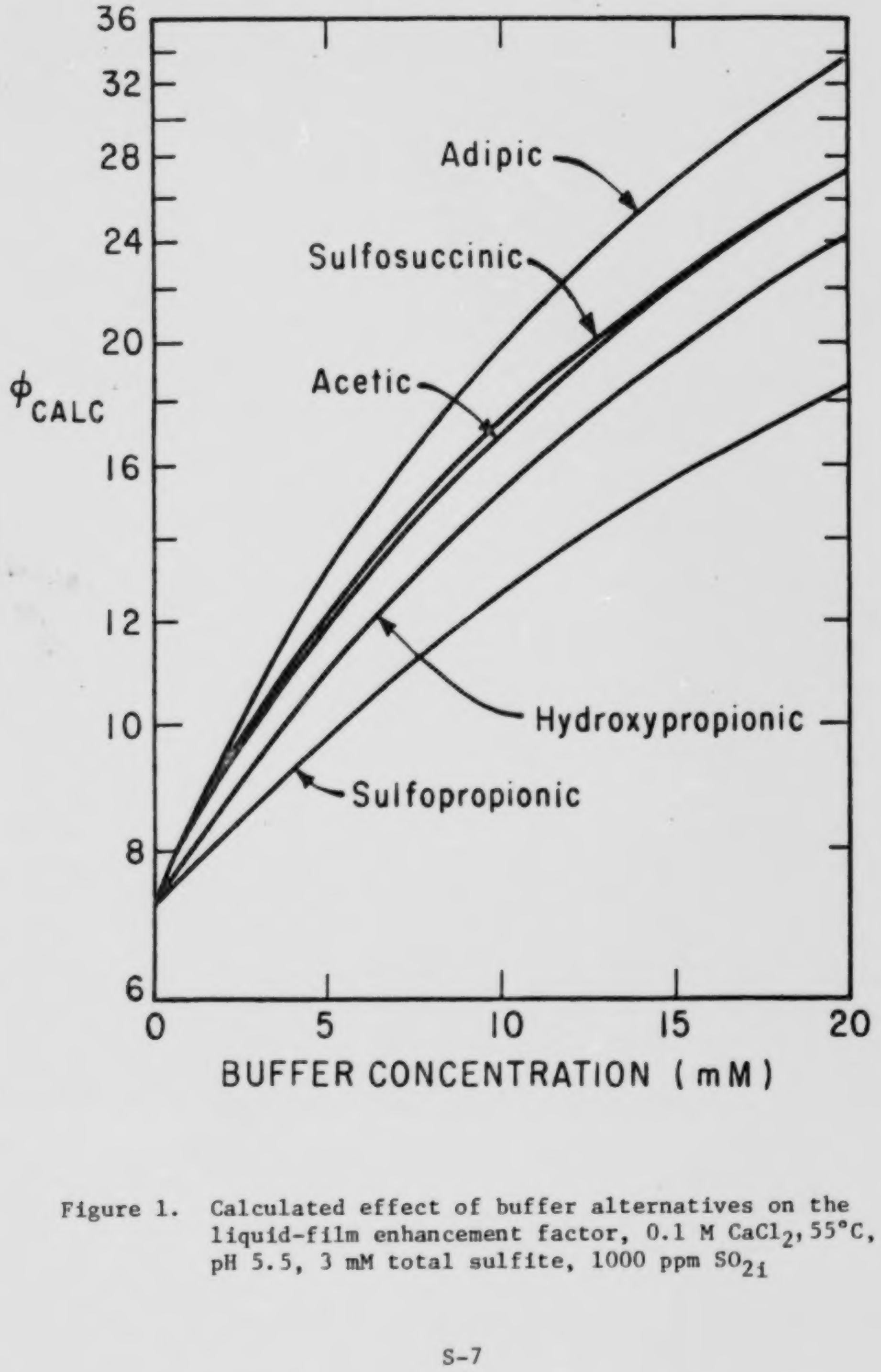

Figure 1. Calculated effect of buffer alternatives on the liquid-film enhancement factor, 0.1 M $CaCl_2$, 55°C, pH 5.5, 3 mM total sulfite, 1000 ppm SO_{2i}

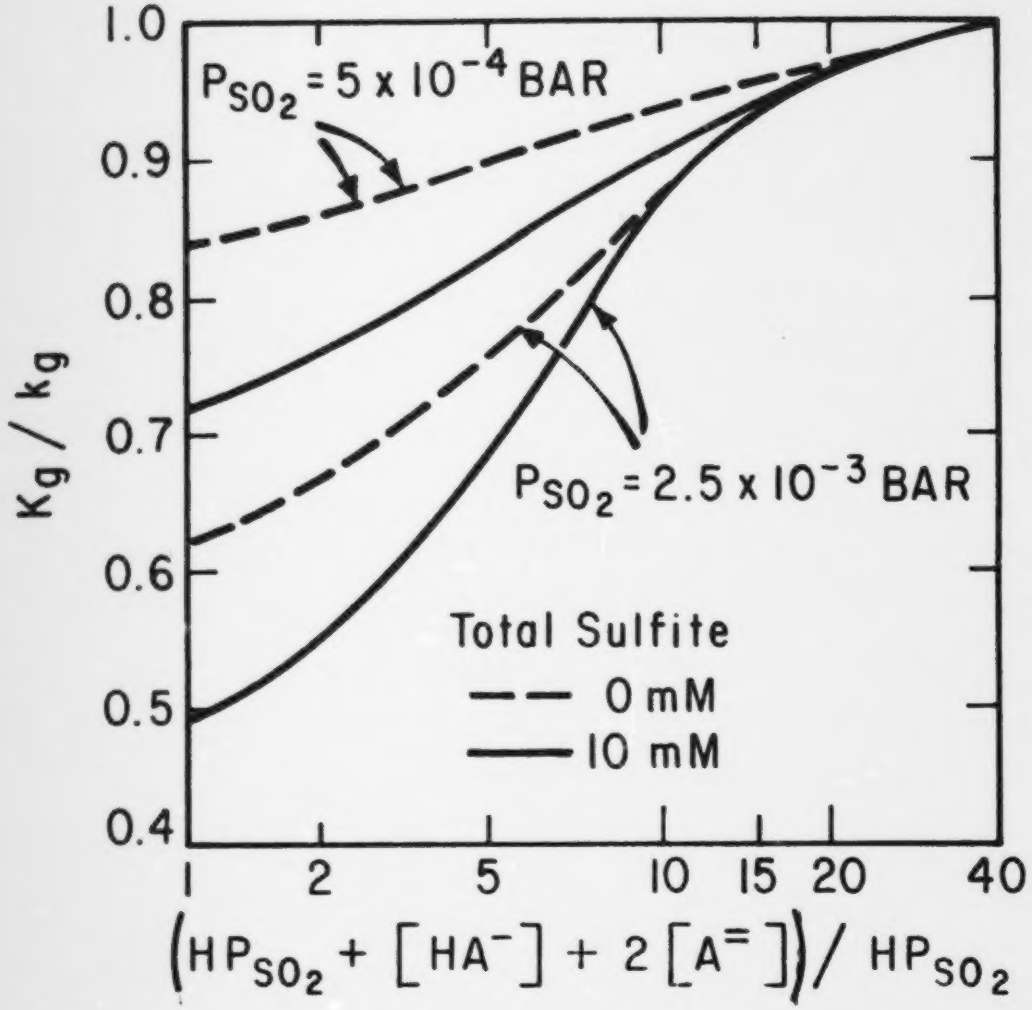

Figure 2: Overall mass transfer enhancement by adipic acid, 55°C, 0.1 M $CaCl_2$, pH 5.

even in the absence of buffer.

In all cases, the curves asymptote to gas phase control with an abscissa value of 10 to 40. 10 mM adipic acid and 10 mM sulfite at pH 5 with 2500 ppm SO_2 gives K_g/k_g of 0.91. This corresponds to an improvement of 1.8 because of adipic acid addition.

Table 1 gives the calculated concentrations of twelve buffers required to get an enhancement factor of 20 in 0.1 M $CaCl_2$ with 10 mM total sulfite at pH 5.0 with 1000 ppm SO_2 at the gas liquid interface. Relative costs have been calculated assuming that makeup rates would be proportional to concentration.

Formic and acetic acids are most attractive, but would probably be volatile under scrubber conditions (Rochelle and King, 1977). Succinic and lactic acids would not be cost-effective if purchased at market price. Fumaric acid is more subject to oxidative degradation. Phthalic and benzoic acids may give undesirable aromatic degradation products. Therefore, the most useful buffers appear to be hydroxypropionic, sulfosuccinic, sulfopropionic, adipic, and hydroxyacetic.

Waste or byproduct organic acids could be cost-effective alternatives. Adipic acid production by nitric acid/oxidation of cyclohexanol/cyclohexanone generates a byproduct consisting of glutaric, succinic and adipic acids which should perform like adipic acid. Air oxidation of cyclohexane to produce cyclohexanone as an intermediate for caprolactam generates a byproduct solution of adipic, hydroxyvaleric, glutaric, and other acids. The performance of this product should be comparable to a mixture of adipic and hydroxypropionic acids.

OXIDATIVE DEGRADATION

Adipic acid and other carboxylic acids are usually stable to oxidation in aqueous solution. However, free radicals generated in the oxidation of hydrocarbons or alcohols will attack carboxylic acids that are present, producing CO_2 and mono or dicarboxylic acids of shorter chain length than the original acid (Denisov et al., 1977).

Such conjugated oxidation of sulfite and adipic acid results in degradation of adipic acid to CO_2 and shorter chain acids such as glutaric and valeric. The rate of degradation is directly proportional to the rate of

Table 1: Relative Costs of Organic Acids,

ϕ = 20, 55°C, pH 5.0, 0.1 M $CaCl_2$, 10 mM total sulfite, 1000 ppm SO_{2i}

Organic Acid	Concentration	Price ($/lb mol)	Relative Cost
Formic	21.1	12.28	0.28
Acetic	15.6	21.62	0.37
Hydroxypropionic	19.7	34.59	0.75
Sulfosuccinic	16.3	43.15	0.77
Sulfopropionic	25.6	34.59	0.97
Adipic	11.8	77.45	1.00
Phthalic	18.1	55.58	1.10
Benzoic	17.9	57.46	1.13
Fumaric	19.1	66.16	1.38
Hydroxyacetic	32.0	39.66	1.39
Succinic	12.3	134.11	1.80
Lactic	34.4	78.82	2.97

sulfite oxidation and the total organic acid concentration ([A]):

$$\frac{d[A]}{dt} = k_d[A]\,\frac{d[SO_3^{=}]_T}{dt}$$

Pilot (Borgwardt, 1979; Chang, 1980), prototype (Head et al., 1979; Burbank and Wang, 1979, 1981, 1982; Wang and Burbank, 1981), and demonstration (Hargrove et al., 1983) plant testing of adipic acid have shown significant levels of degradation. The degradation losses are generally reduced at pH less than 5.0 and increased by forced oxidation.

The objective of this work was to quantify the rates and products of the degradation of adipic acid and alternative carboxylic acids. Parallel work by Radian Corp. (Meserole et al., 1979; Meserole et al., 1980; Terry et al., 1982; Jarvis et al., 1982) has measured rates and products of adipic acid degradation.

In this work, degradation of 5 to 20 mM carboxylic acid has been measured during batch oxidation of 1 to 2 M $CaSO_3$ slurry at 55°C with pure oxygen sparged into an agitated reactor. Slurry was analyzed for total sulfite by iodine titration. Filtered solution was analyzed for specific carboxylic acids by ion chromatography or ion exclusion chromatography. Additional solution analyses were performed by gas chromatography with extraction into chloroform before and after aqueous methylation.

Figure 3 gives typical results on the rate of sulfite oxidation. At pH 4.3 or 4.5 or with 1 mM Mn, the sulfite oxidation rate was at a maximum value, limited by either mass transfer or the supply of O_2 to the reactor. Without Mn, the sulfite oxidation rate decreased with increasing pH and essentially stopped at pH 6.0.

Both hydroxycarboxylic acids and thiosulfate inhibited sulfite oxidation. At pH 5.0, 0.3 mM Mn was sufficient to compensate for inhibition by 10 mM hydroxyacetic acid. With 1 mM Mn, sulfite oxidation was completely inhibited by 2 mM thiosulfate at pH 5.5 and 3 mM thiosulfate at pH 5.0. 10 mM thiosulfate was insufficient to inhibit sulfite oxidation at pH 5.0 in the presence of 1 mM Mn and 0.3 M $MgSO_4$.

Figure 4 gives the degradation rate constant (k_d) of adipic acid as a function of pH with and without Mn. In the absence of Mn, k_d is only a weak function of pH. With 1 mM Mn, k_d is significantly reduced and is a strong function of pH. At pH 4.5, the degradation of succinic acid was almost

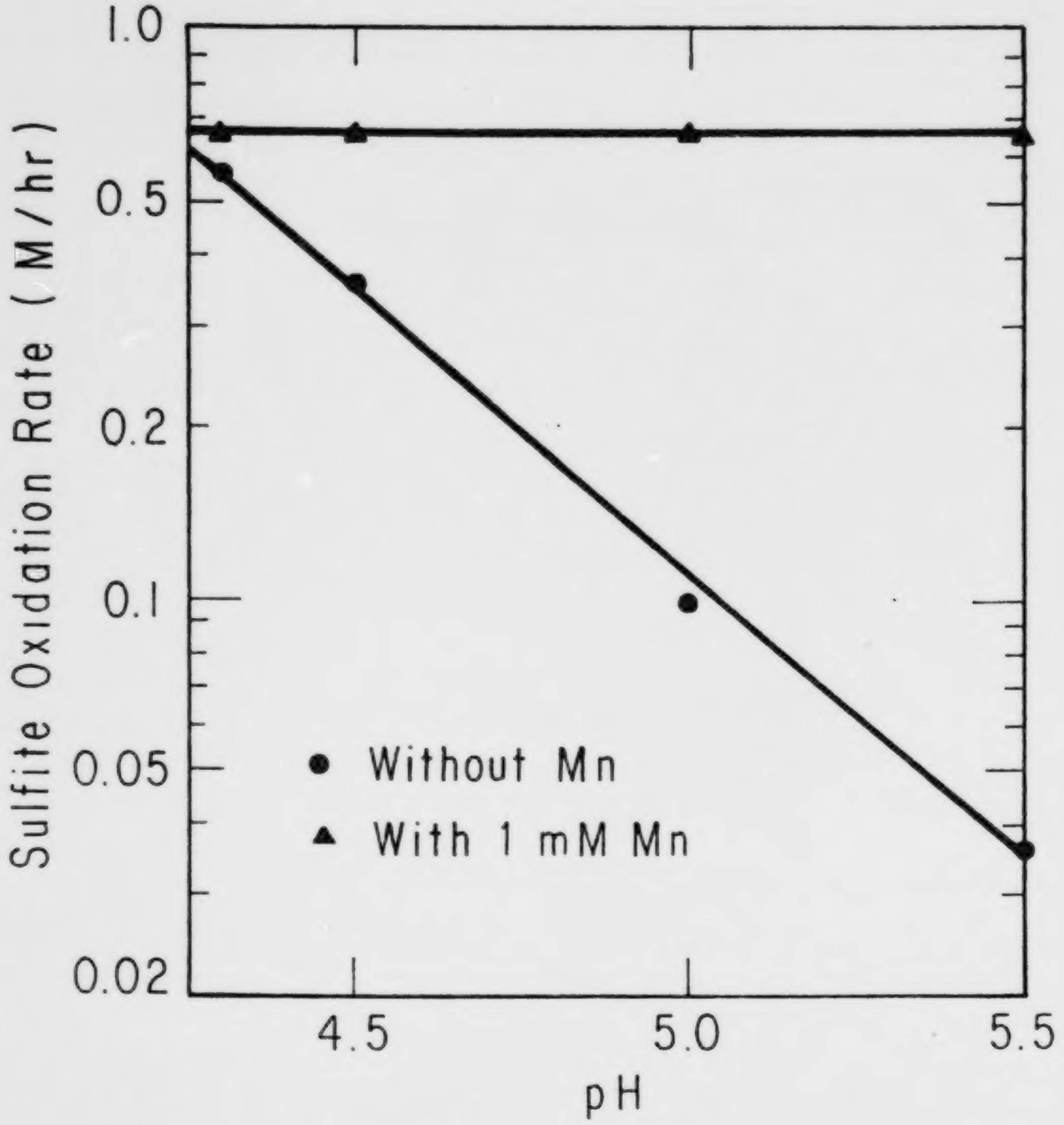

Figure 3 Effect of pH on Sulfite Oxidation
1340 rpm, 200 ml O_2/min.

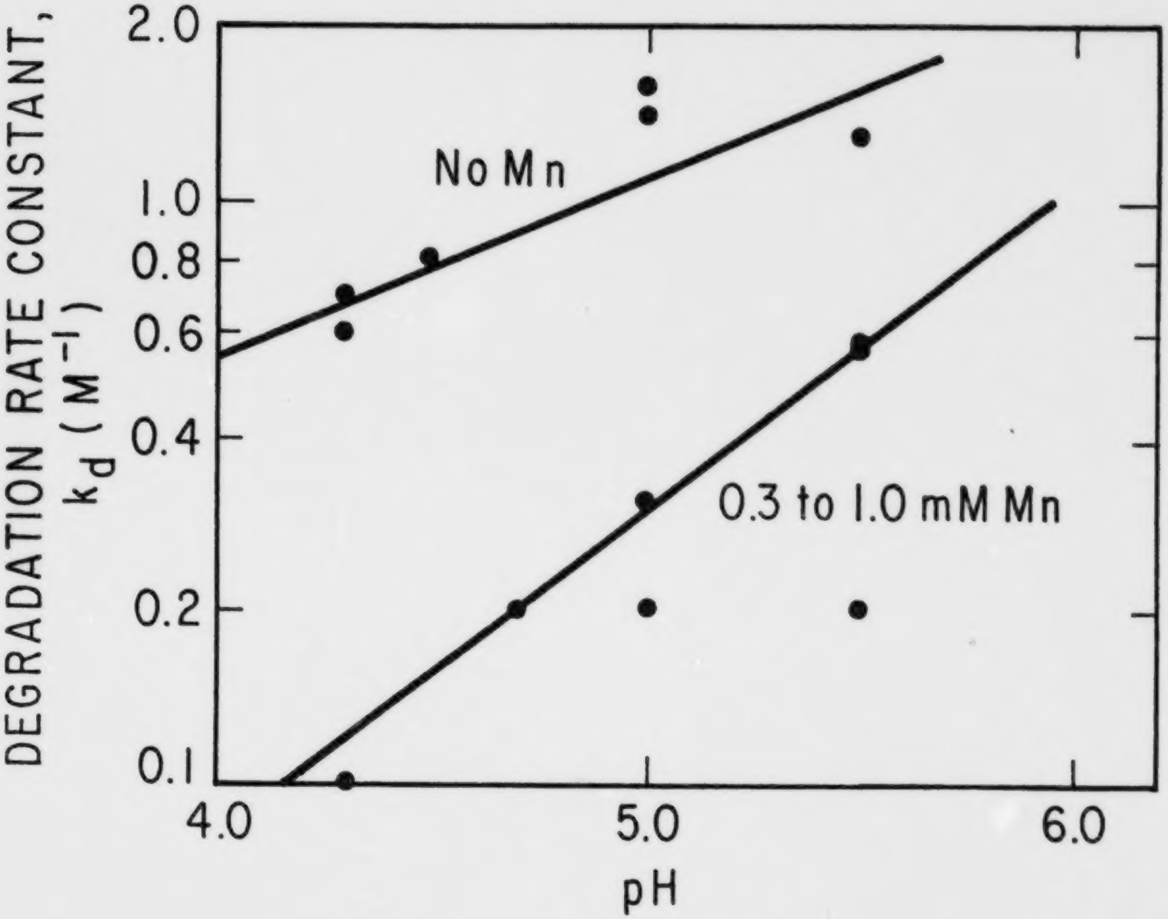

Figure 4: Adipic Acid Degradation

completely inhibited by 0.3 mM Mn, but hardly affected by 0.2 mM Mn.

These data are generally consistent with degradation rates measured at the Shawnee 10 MW test facility (Burbank and Wang, 1982) and at the Radian bench-scale scrubber (Jarvis et al., 1982).

No adipic acid degradation was observed in experiments with no sulfite oxidation, resulting from high pH or the presence of hydroxyacids or thiosulfate. At pH 5.5, with 1 mM Mn, the presence of 1 mM thiosulfate reduced k_d from 0.6 to 0.25 M^{-1}, while hardly affecting the rate of sulfite oxidation.

Table 2 gives a comparison of degradation rate constants as measured for 8 organic acids. The aliphatic acids (succinic, glutaric) and sulfoacids (sulfopropionic, sulfosuccinic) behaved much like adipic acid. Dibasic waste acid (mostly glutaric) also degraded like adipic. Fumaric acid degraded much faster than adipic acid because of its carbon-carbon double bond. The hydroxyacids both degraded much slower, probably because of the alcohol function. In one experiment with a mixture of hydroxyacetic and adipic acids, the adipic acid degraded as usual, but the hydroxyacetic acid degraded much slower than adipic acid.

Table 3 gives the typical degradation products of adipic acid at pH 5.0 with and without Mn. With Mn, there are nominal concentrations of the expected products, valeric and glutaric acids. Without Mn, there is also an appreciable accumulation of the aldehyde-acid, 4-carboxybutanal. In both cases most of the adipic acid that degrades is probably lost as CO_2.

CONCLUSIONS

1. Adipic acid has attractive buffer properties, and it is cost-effective, non-toxic, and commercially available in large quantities. It coprecipitates with $CaSO_3$ and is subject to oxidative degradation, but these problems should be minimized by using forced oxidation at low pH with high concentrations of dissolved Mn.

2. Byproduct dibasic acid (DBA) containing primarily glutaric acid is a cost-effective alternative equivalent to adipic acid.

3. The hydroxycarboxylic acids are uniquely inert to oxidative degradation and inhibit sulfite oxidation in the absence of Mn. Hydroxypropionic acid is economically attractive; however, its synthesis from acrylic acid

Table 2: Measured Degradation Rate Constants of Buffer Alternatives

	pH	Mn (mM)	k_d (M^{-1})
Adipic	4.5	0.0	0.8
		1.0	0.15
	5.5	0.0	1.6
		1.0	0.6
Glutaric	5.5	0.1	1.6
Succinic	4.5	0.0	0.5
Sulfopropionic	5.0+	0.0	1.0
Sulfosuccinic	5.0+	0.0	1.0
Fumaric	5.5	1.0	2.4
Hydroxyacetic	5.0	0.3	0.1
Hydroxypropionic	4.5	0.0	0.2

Table 3: Organic Acids in a solution of 10 mM Adipic Acid Degraded at pH 5.0

	Concentrations (mM)	
Mn	0.1	3.0
Adipic	1.40	5.20
Glutaric	0.55	0.45
Unknown 117 (C5)	0.50	-
4-Carboxy-butanal	2.50	0.04
Succinic	0.20	0.04
Malonic	0.50	-
Valeric	0.09	0.50
Unknown 422 (C4)	0.40	0.03
Butyric	0.06	0.03
Carbon lost (CO_2)	29.3	23.5

gives polyacrylic acid impurities that would probably have to be separated. Glycolic acid is commercially available but economically somewhat less attractive.

4. Sulfosuccinic acid is economically attractive when synthesized *in situ* or offsite from maleic anhydride. It is subject to oxidation, but should give nonvolatile degradation products.

5. Basic aluminum salts are ineffective for mass transfer enhancement.

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SECTION 1

SYNTHESIS OF ORGANIC ACIDS FOR STACK GAS DESULFURIZATION BY AQUEOUS SCRUBBING

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THESIS
Presented to the Faculty of the Graduate School of
The University of Texas at Austin
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for the Degree of

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May 1981

SECTION 1

ABSTRACT

Reaction kinetics and design concepts are presented for the commercial synthesis of sulfopropionic, sulfosuccinic, and β-hydroxypropionic acids. These buffers have been proposed as mass transfer additives for flue gas desulfurization by $CaO/CaCO_3$ slurry scrubbing. Rates for the addition of bisulfite to unsaturated acids were measured at 25 to 55°C, pH 2 to 12, and ionic strength 0.35 to 2.10 N. Second-order rate constants and activation energies for reaction of bisulfite with acrylic, fumaric, and maleic acids at pH 5, 55°C, and ionic strength 0.5 N were respectively: 0.21 $M^{-1}min^{-1}$, 14 kcal/gmol; 0.031 $M^{-1}min^{-1}$, 6.1 kcal/gmol; and 0.52 $M^{-1}min^{-1}$, 17 kcal/gmol. The rate constants were independent of pH from 4 to 7 but increased with ionic strength. Rates for the hydration of acrylic acid were measured at 100 to 140°C with catalysis by 0.1 to 2 M H_2SO_4 or by a H^+ loaded ion resin. At 100°C the second-order rate constant was 0.11 $M^{-1}min^{-1}$ with an activation energy of 17 kcal/gmol.

For commercial applications, acrylic acid and maleic anhydride could be sulfonated with bisulfite in the scrubber or with Na_2SO_3 in an offsite reactor. Fumaric acid is not a viable starting material. Acrylic acid would have to be hydrated in an offsite reactor near 100°C with H_2SO_4 or H^+ loaded resin catalyst.

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CHAPTER 1-1

INTRODUCTION

Since the 1960's SO_2 air pollution has become a serious environmental concern. The primary source of SO_2 emissions is coal-fired power plants (Bondor, et al. 1977). Of the several different methods suggested for reducing SO_2 emissions, flue gas desulfurization (FGD) is the only available commercial process.

There are two types of FGD systems: 1) throwaway scrubbing, and 2) regenerable scrubbing processes. Only throwaway scrubbing has achieved any commercial success. In throwaway scrubbing SO_2 is absorbed in an aqueous solution or slurry and disposed of in a landfill as a waste solid of $CaSO_3$/$CaSO_4$. A typical regenerable process absorbs SO_2 gas. This research is concerned primarily with simple slurry scrubbing (Figure 1-1). In the scrubber the SO_2 is absorbed in an aqueous slurry of $CaSO_3/CaSO_4$ and excess lime (CaO) or limestone ($CaCO_3$). The CaO or $CaCO_3$ is needed to neutralize the acidic SO_2. The slurry flows into the crystallizer where CaO or $CaCO_3$ is added and $CaSO_3/CaSO_4$ precipitated. Most of the slurry is recycled to the scrubber. A small portion of the recycle is fed to the solid/liquid separator. The liquid is recycled to the scrubber while the solid waste product is discarded.

The solubility of SO_2 in water is quite low. Flue gas containing 2000 ppm SO_2 will have an equilibrium concentration of less than 1 mM in the liquid phase (Epstein, 1975) which would require a large liquid flow rate through the scrubber. To remove the SO_2 efficiently a source of alkalinity is needed to neutralize the SO_2:

$$SO_2 + OH^- \longrightarrow HSO_3^-$$

In the simple slurry scrubbing process this can be provided by the dissolution of $CaSO_3$ or excess $CaO/CaCO_3$ (Rochelle, 1977):

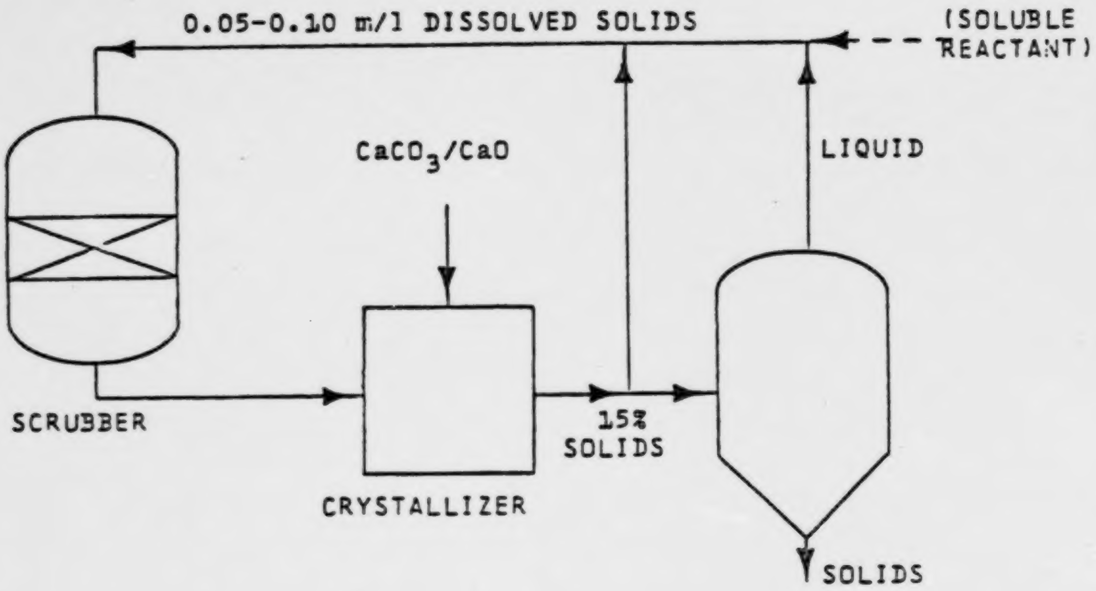

0.05-0.10 m/l DISSOLVED SOLIDS
(SOLUBLE REACTANT)
CaCO3/CaO
LIQUID
SCRUBBER
15% SOLIDS
CRYSTALLIZER
SOLIDS

Figure 1-1. Simple Slurry Scrubbing

$$CaSO_3 + SO_2 + H_2O \longrightarrow Ca^{++} + 2HSO_3^-$$

$$CaCO_3 + 2SO_2 + H_2O \longrightarrow Ca^{++} + 2HSO_3^- + CO_2$$

$$CaO + 2SO_2 + H_2O \longrightarrow Ca^{++} + 2HSO_3^-$$

In this system the alkalinity is dependent upon the solids solubility and the pH. To improve SO_2 mass transfer from the gas to the liquid phase a method is needed to provide alkalinity at the interface. There are two suggested methods: 1) soluble alkali additives, and 2) organic acid buffers (Rochelle, 1977). This work is concerned with the production of useful organic acid buffers.

The use of soluble alkalis or acid buffers has been shown to enhance SO_2 removal (Chang, 1979). For existing designs use of the above additives can increase SO_2 removal from 85% to 95% or better. This is quite attractive since no process changes or large capital expenditures are needed. The only expenses are material and handling costs. In the design of new plants additional benefits are possible such as reducing the size of the scrubber required. Advantage can also be taken of reduced pressure drop and lower flow rates, thereby reducing operating and capital costs. One objective of this work is to determine the cost to the power plant or designer of using organic acid buffers.

ORGANIC ACID BUFFERS

Organic acids enhance SO_2 removal by the following reaction,

$$SO_2 + H_2O + A^- \longrightarrow HSO_3^- + HA$$

where A^- is the unprotonated species and HA is the protonated acid. To be effective a buffer must function as an alkali under scrubber conditions. The additive should have significant buffer capacity between the pH of the gas-liquid interface in the scrubber, typically 3 to 3.5, and the pH of the bulk liquid, typically 5 to 5.5. Therefore the pK_a should be between 3.0 and 5.0. As little as 10 to 20 mM of organic acid can provide the maximum effect on mass transfer. This is the most important but not the only consideration for the possible use of an organic acid as a buffer additive.

Some important additional considerations for an organic acid are 1) cost, 2) volatility, and 3) degradation. The cost of some acids relative to adipic acid is shown in Table 1-1. The acid alternatives are compared to adipic acid because adipic acid has been extensively tested in pilot plant work (Borgwardt, 1978). The costs shown are a function of concentration needed in the scrubber and the purchase price per lb mole only. From the table it would appear that acetic acid would be an ideal buffer. Unfortunately, under scrubber conditions, acetic acid is quite volatile which could produce a noticeable odor and raise environmental concerns. Phthalic and benzoic acids have not been pursued since their presence in the waste solids could present a pollution problem due to their aromatic nature. Succinic and lactic acids can be eliminated because of their high cost.

The remaining acids, sulfosuccinic, sulfopropionic, and hydroxypropionic, have attractive relative costs. Unfortunately these acids are not available commercially and would have to be produced by the user or by an offsite contractor. The relative cost given does not reflect this fact.

The three acids discussed above contain either a sulfonic or hydroxy group which make the acid essentially nonvolatile under scrubber conditions. This can represent a substantial savings by reducing makeup costs. Also, these groups reduce the volatility of any degradation products and likewise reduce makeup costs. The degradation rate of these acids has been shown to be about the same as for adipic acid (Garcia, 1980). Also, hydroxypropionic acid is a sulfite oxidation inhibitor (Garcia, 1980) which should reduce acid degradation.

The objectives of this work are 1) to measure reaction rate constants for the synthesis of sulfopropionic, sulfosuccinic, and hydroxypropionic acids, and 2) to develop process concepts for the production of these acids. The reaction rates will be measured as a function of temperature, pH, and ionic strength of the solution. Using the experimental rate constants, process concepts will be developed to economically produce the organic acids.

SYNTHESIS

Possible synthesis paths for sulfopropionic, sulfosuccinic, and hydroxypropionic acids are shown in Figure 1-2. The unsaturated acids, acrylic, maleic, and fumaric, sulfonate at room temperature in the presence of bisulfite (Keller, 1950; Cavanaugh, 1978). The reversible hydration of acrylic acid to produce hydroxypropionic acid requires acid catalysis and

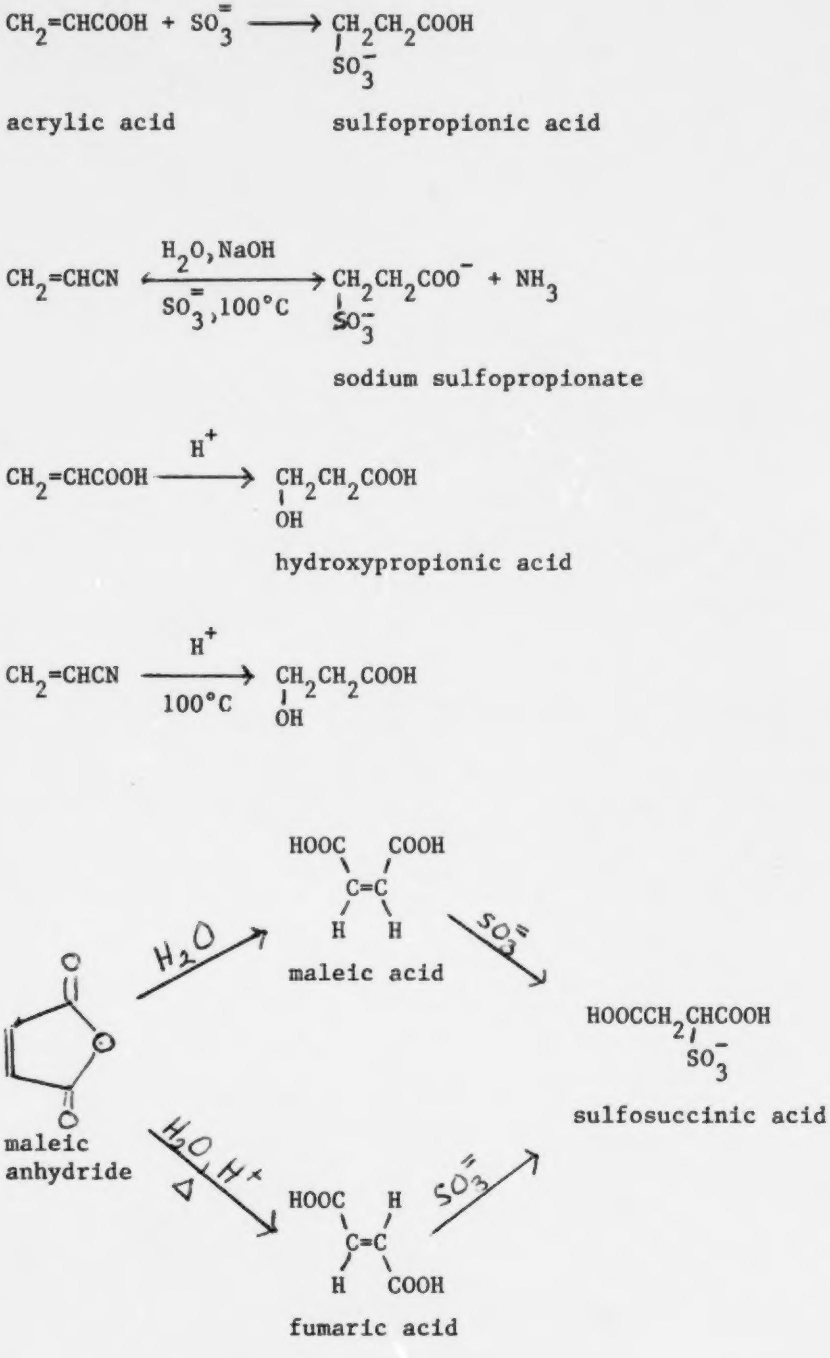
Table 1-1: Relative Buffer Costs

Acid Buffer	Buffer conc.[a] needed (mM)	Price %/lbmol	Relative[b] cost
acetic	12.3	21.6	0.37
adipic	9.5	75.3	1.00
sulfosuccinic	12.2	43.2	0.74
sulfopropionic	20.6	30.6	0.88
hydroxypropionic	14.3	30.6	0.74
phthalic	14.6	55.6	1.13
succinic	8.4	134.1	1.58
benzoic	14.2	57.5	1.14
lactic	23.8	78.8	2.62

---

[a] Enhancement factor = 20, 0.3 M $CaCl_2$, pH 5.0, 10.0 mM $[SO_3^=]_T$,
$P_{SO2} = 10^{-3}$ Bar, (Weems, 1980)

[b] Relative cost = (price/lbmol of acid X acid conc. needed) -
(price/lbmol of adipic acid X adipic acid conc. needed)



$$CH_2{=}CHCOOH + SO_3^{=} \longrightarrow \underset{SO_3^-}{\underset{|}{C}}H_2CH_2COOH$$

$$CH_2{=}CHCN \xrightarrow[SO_3^{=},\,100°C]{H_2O,\,NaOH} \underset{SO_3^-}{\underset{|}{C}}H_2CH_2COO^- + NH_3$$

$$CH_2{=}CHCOOH \xrightarrow{H^+} \underset{OH}{\underset{|}{C}}H_2CH_2COOH$$

$$CH_2{=}CHCN \xrightarrow[100°C]{H^+} \underset{OH}{\underset{|}{C}}H_2CH_2COOH$$

$$HOOCCH_2\underset{SO_3^-}{\underset{|}{C}}HCOOH$$

acrylic acid
sulfopropionic acid
sodium sulfopropionate
hydroxypropionic acid
HOOC COOH
C=C
H H
maleic acid
H_2O
$SO_3^{=}$
maleic anhydride
H_2O, H^+
Δ
HOOC H
C=C
H COOH
fumaric acid
$SO_3^{=}$
sulfosuccinic acid

Figure 1-2: Synthesis methods for organic acids

elevated temperatures (Cavanaugh, 1978).

Acrylonitrile is cheaper than acrylic acid and should be economically more attractive for the production of the propionic acids. Unfortunately acrylonitrile is carcenogenic and can present a serious health hazard making its presence in the scrubber environmentally unacceptable. Therefore, any unreacted acrylonitrile would have to be removed from the product stream. This would increase production costs and probably make acrylic acid the cheaper starting material. Acrylic acid and maleic anhydride are also somewhat toxic, but can be adequately converted to nontoxic products.

A few other acids and synthesis methods should be mentioned. Chloroacids could be a possible starting material for sulfonic or hydroxy acids by means of a simple substitution reaction. These acids are toxic and not available at an attractive price, making this synthesis method unlikely. Diglycolic acid has good pK_a values and should be a candidate. Even though diglycolic acid is not available commercially, diethylene glycol could be added to the scrubber where it may undergo the following oxidation reaction:

$$HOCH_2CH_2OCH_2CH_2OH \longrightarrow HOOCCH_2OCH_2COOH$$

However, a literature survey (Lloyd, 1956) indicates the major oxidation product would be formic acid. Diglycolic acid could be produced in a separate reactor using nitric acid as the oxidant. There are several patents on this process (Schroader, 1977; Miya, 1977; Kiyoura, 1976).

Previous work (Cavanaugh, 1978; Schenck and Danishefsky, 1951; Hall and Stern, 1950) on the synthesis of sulfopropionic, sulfosuccinic, and hydroxypropionic acids has provided little quantitative data on the reaction rates as a function of such variables as pH, temperature, and ionic strength. Knowledge of the rates is necessary to the development of possible process concepts for the production of these acids. Therefore, one objective of this work is to determine rate constants as a function of temperature, pH, and ionic strength of the solution. The reason for this choice of variables will be discussed below.

The second objective of this work is the development of process concepts for the production of sulfopropionic, sulfosuccinic, and hydroxypropionic acids. The production of the sulfonic acids can be divided into two distinct categories, 1) *in situ* sulfonation, and 2) offsite production. *In situ* sulfonation is economically the most attractive method for production of the acid. The starting material, acrylic acid, maleic anhydride, or fumaric acid, is added to the scrubber where the acid undergoes sulfonation. The residence time for a reasonable conversion must be less than the residence time of the scrubber system. This is particularly important for acrylic acid and maleic anhydride because of the health hazards these compounds may present. Fumaric acid is a food additive and therefore environmentally of no concern if it is discarded. Fumaric acid has one pK_a value which makes it useful as a buffer additive. Unless degradation losses are substantial, a loss of fumaric acid in the waste solids will not be a serious problem.

In situ production requires no more capital or labor costs than the use of adipic acid and therefore Table 1-1 is a good comparison to the costs of using adipic acid. To determine if the residence time of the scrubber system is adequate, the sulfonation rate constant must be known at scrubber conditions: 55 C, pH 4 to 6, 1 to 20 mM total dissolved sulfite, with up to 0.1 M dissolved calcium.

Offsite production would be required if *in situ* sulfonation is not feasible. This could occur if the rate constant does not allow a smaller residence time and/or the volatility and degradation losses of the unreacted acid are unacceptable.

The variables which are important for *in situ* sulfonation are also important for offsite production. Offsite production is the use of a separate reactor at the power plant location or at a contractor's plant. The producer would need to know the rate constant as a function of temperature to determine the residence time required at any temperature to achieve the desired conversion level. Due to rising energy costs the reaction would probably be carried out at ambient temperature.

If offsite sulfonation is performed at the power plant, there are two possible sources of sulfite, 1) $CaSO_3$ slurry from the scrubber, and 2) Na_2SO_3. In the first case it must be determined if sulfonation is possible in the slurry and, if not, is it possible to make a simple and inexpensive change to allow sulfonation. Use of the $CaSO_3$ is attractive because no source of sulfite must be purchased. The only additional capital expense is the cost of a reactor. If the slurry cannot be used, Na_2SO_3 can be purchased and used as a source of sulfite. For both methods the type of reactor selected will depend on minimizing energy and capital costs and ease of operation. If the sulfonation is done at the power plant site, a simple production scheme would be important.

As stated previously the hydration of acrylic acid to hydroxypropionic acid is reversible and requires elevated temperatures and H^+ catalysis, such as sulfuric acid. Acrylic acid undergoes polymerization at high temperatures and high concentrations. This side reaction can be reduced by increasing the concentration of the catalyst. Sulfuric acid concentration and temperature will determine the hydration rate constant and should be optimized to minimize total energy and capital costs.

The results obtained will be important in considering the use of sulfopropionic, sulfosuccinic, or hydroxypropionic acids as buffer additives. Production of the acid economically will be a factor in the further consideration of these acids. Other criteria must be investigated before a final decision can be made on the use of these organic acids.

CHAPTER 1-2

SULFONATION OF ACRYLIC, FUMARIC, AND MALEIC ACIDS

INTRODUCTION

The use of sulfopropionic and sulfosuccinic acids has been shown to increase sulfur dioxide removal efficiency (Weems, 1980). These two acids satisfy three additional criteria, 1) low volatility, 2) low cost, and 3) nonvolatile degradation products. Under scrubber conditions the sulfonic acid group is dissociated, leaving the acid in a nonvolatile, charged state. The sulfonic acid group will also tend to make degradation products nonvolatile. The sulfonic acids compare economically with adipic acid. The rate of degradation of the sulfonic acids is about the same as the degradation rate of adipic acid (Garcia, 1980).

Since neither sulfopropionic or sulfosuccinic acid are available commercially, an economical production scheme must be devised before these acids can compete with adipic acid. The production of these acids may be accomplished by either of two methods, 1) *in situ* sulfonation, or 2) offsite production. Dissolved sulfite is present in the scrubber and can be used to produce the sulfonic acids by simply adding the starting material to the scrubber system. If this is not a reasonable method due to volatility or degradation of the starting material, then sulfonation can be accomplished offsite in a separate reactor. Before either method can be chosen, the sulfonation rate constant must be known as a function of temperature, pH, and ionic strength.

The rate constant at 55°C, the operating temperature of the scrubber, will determine the conversion to the sulfonic acid available in the scrubber system. Insufficient conversion can lead to several problems. If sulfopropionic acid is used this will necessitate more acrylic acid initially to produce the required concentration of sulfopropionic acid. This will mean an increased amount of acrylic acid stripped into the flue gas and more acrylic acid in the waste solids. Both of these two situations are environmentally unacceptable.

If the conversion of fumaric acid is inadequate then the amount may also have to be increased, since fumaric acid is somewhat less effective for mass transfer enhancement than sulfosuccinic acid. Since fumaric acid is nonvolatile, this will not be a problem. Also, fumaric acid is a food additive and therefore environmentally safe. The only problem will be the additional cost for the fumaric acid lost in the waste solids. Depending on the magnitude of the rate constant this may or may not be cheaper than offsite production.

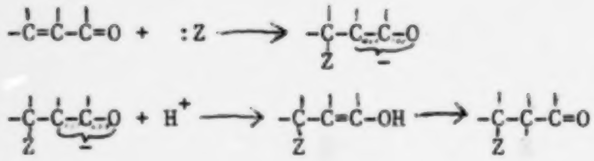
Maleic anhydride is a strong irritant because moisture hydrolyzes the anhydride to the acid which causes burns. Therefore maleic anhydride dust is very dangerous (Merck Index, 1976). The use of maleic anhydride at the plant will depend on the power plant taking the necessary material handling precautions. An additional problem is the loss of maleic acid from the scrubber system. Fortunately maleic acid is nonvolatile under scrubber conditions. If the sulfonation rate constant is large then sufficient in situ sulfonation will be possible and the presence of maleic acid in the waste solids will not be significant.

If in situ sulfonation is not feasible, then offsite production is the other alternative. Two sources of sulfite could be used, $CaSO_3$ or Na_2SO_3. The ionic strength of the solution due to Na^+ or Ca^{++} will affect the rate constant. The pH of the solution may also be important. If the sulfonation rate is highly pH-dependent the reactor volume could be minimized by raising or lowering the pH. It is also important to know the rate constant as a function of temperature. Due to the high cost of energy the optimum operating temperature will probably be ambient.

LITERATURE REVIEW

The nucleophilic addition to α,β-unsaturated compounds produces α,β-substituted carbonyl compound. Some compounds which have been studied are unsaturated esters, nitriles, aldehydes, ketones, and carboxylic acids (Morton, 1951; Zanden, 1927; Hori, 1942; Knoevenagel, 1904). Typical addition groups are CN^-, $SO_3^=$, and ammonia or certain derivatives of ammonia.

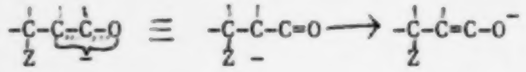
The reaction is believed to take place by the following mechanism (Morrison and Boyd, 1973):



$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O + :Z \longrightarrow -\underset{Z}{\overset{|}{C}}-\underbrace{\overset{|}{C}\cdots\overset{|}{C}\cdots O}_{-}$$

$$-\underset{Z}{\overset{|}{C}}-\underbrace{\overset{|}{C}\cdots\overset{|}{C}\cdots O}_{-} + H^{+} \longrightarrow -\underset{Z}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}-OH \longrightarrow -\underset{Z}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\overset{|}{C}=O$$

The nucleophilic reagent adds to the β position of the carbon-carbon double bond to form the most stable anion which is shown below:



$$-\underset{Z}{\overset{|}{C}}-\underbrace{\overset{|}{C}\cdots\overset{|}{C}\cdots O}_{-} \equiv -\underset{Z}{\overset{|}{C}}-\underset{-}{\overset{|}{C}}-C=O \longrightarrow -\underset{Z}{\overset{|}{C}}-\overset{|}{C}=C-O^{-}$$

This intermediate enables the electronegative oxygen to accommodate the negative charge. The addition to α,β-unsaturated carbonyl compounds is possible because of the above resonance stabilized anion. Unconjugated systems do not form this stable intermediate and therefore do not readily undergo addition by the above mechanism but instead by a free radical mechanism (Schenck, 1951).

The production of sulfocarboxylic acids can be accomplished by using either nitriles or unsaturated acids (Cavanaugh, 1978). The reaction rate is second order overall and is given by the following equation:

$$r = k[SO_3^{=}][acid] \qquad 1\text{-}1$$

where brackets indicate total concentrations (such as $SO_3^{=}$ and HSO_3^{-}). Important variables affecting the rate of sulfonation are 1) temperature, 2) pH of the reaction solution, and 3) ionic strength of the solution.

Studies on nitriles and esters have yielded activation energies which follow the Arrhenius equation with values between 10 and 20 kcal/gmol (Morton and Landfield, 1952). The activation energy for the ester is less than the nitrile because the stability of the ester intermediate is greater than the nitrile intermediate.

Schenck's (1951) data indicates the sulfonation of acrylic acid occurs such that the intermediate species has a -2 charge. The reaction would be between $SO_3^{=}$ and acrylic acid or between HSO_3^{-} and acrylate. On the basis of reaction with esters and nitriles, $SO_3^{=}$ is more reactive than HSO_3^{-} (Morton and Landfield, 1952). The sulfonation of maleic or fumaric acid could have an intermediate with a -3 or -4 charge (acid + $SO_3^{=}$). The effect of ionic strength would become greater as the charge on the intermediate increases.

The last reaction variable is the ionic strength of the solution. The addition of bisulfite occurs by a $S_N{}^2$ mechanism which is known to be affected by the ionic strength of the solution. The effect of ionic strength on rate constants of ionic reactions can be expressed by the following equation (Bronsted, 1922; Guntleberg, 1926; Christianson, 1952):

$$\log \frac{k}{k_o} = (Z_P^2 - Z_R^2) \frac{(I)^{1/2}}{1 + (I)^{1/2}} \qquad 1\text{-}2$$

where k = rate constant

k_o = rate constant at infinite dilution

Z_P = charge on product

Z_R = charge on reactant

I = ionic strength

The ionic strength I, is defined by the following:

$$I = \tfrac{1}{2} \Sigma m_i Z_i^2 \qquad 1\text{-}3$$

where the summation is over all the ionic species, Z_i, with a molal concentration of m_i. The rate of reaction between two anions has been shown to be a function of the cation concentration (Olson and Simpson, 1949). For the sulfonation of a monocarboxylic acid, $Z_p{}^2 = 4$, $Z_r{}^2 = 2$ and the salt effect equation becomes:

$$\log \frac{k}{k_o} = 2 \frac{(I)^{1/2}}{1 + (I)^{1/2}} \qquad 1\text{-}4$$

Changing the ionic strength of the solution from 0.1 M NaCl to 1.0 M NaCl increases the rate constant by a factor of 3.3. The reaction of a dicarboxylic acid is more complicated because the reacting species may have a charge of zero, -1, or -2. With a charge of -2 on the acid and -2 on the sulfite the dependence is:

$$\log \frac{k}{k_o} = 8 \frac{(I)^{1/2}}{1 + (I)^{1/2}} \qquad 1\text{-}5$$

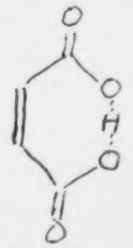
Changing the concentration of NaCl in a reaction solution from 0.1 M to 1.0 M will change the rate constant by a factor of 120.

Divalent cations such as Mg^{++} and Ca^{++} are believed to have a greater effect on the rate constant than monovalent cations (Fava and Bresadola, 1955). The divalent cation complexes more strongly with the acid thereby producing a more stable intermediate than is possible with a monovalent cation. The stable intermediate produces a larger rate constant.

The only available data on the sulfonation of acrylic acid made no attempt to determine the effect of pH or ionic environment on the reaction rate. At 30°C the rate constant for the reaction between $NaHSO_3$ and NaA varied from 0.76 $M^{-1}sec^{-1}$ to 0.29 $M^{-1}sec^{-1}$ (Hagglund, 1926). The author postulated the experimental variation was due to the polymerization of acrylic acid. Since the acrylic acid used was produced from dibromopropionic acid without added polymerization inhibitor, polymerization could certainly be a problem. The experimental rate constant was based on sulfite disappearance and therefore not as great as it would have been due to the smaller amount of acrylic acid present. The experiments for our work were performed with acrylic acid supplied with added polymerization inhibitor.

The rate constant for the sulfonation of maleic and fumaric acids to sulfosuccinic acid (Hagglund, 1926) have also been measured. Again no dependence on pH or ionic environment was determined. At 80°C the rate constants were 0.086 $M^{-1}sec^{-1}$ for fumaric acid and bisulfite and 0.16 $M^{-1}sec^{-1}$ for maleic acid and bifulsite.

Maleic acid can form the following species in solution (Encycl. of Chem. Tech., 1972):



Because fumaric acid is the trans isomer the H bonding is not possible as with maleic acid. Therefore in aqueous solution maleic acid is a much stronger acid than fumaric acid. The pK_a values of maleic and fumaric acids are respectively, 1.8, 6.0, and 3.3, 4.4. Apparently the H bonding produces a more stable intermediate and therefore accounts for the faster sulfonation of maleic acid as compared to fumaric acid.

There is some limited data on the pH dependence of fumaric and maleic acid sulfonation at 25°C (Zanden, 1927). The experiments reacted equimolar 0.05 M unsaturated acid and SO_2 with NaOH/acid ratios of one, two, and three to give low, medium, and high pH values. The data are listed below with estimated pH values:

acid	$NaOH/H_2A$	approx. pH	$k(M^{-1}min^{-1})$
fumaric	1	2-3	$59x10^{-5}$
	2	3-5	$19x10^{-4}$
	3	6-9	$53x10^{-5}$
maleic	1	2-3	$112x10^{-5}$
	2	3-5	$40x10^{-4}$
	3	6-9	$60x10^{-3}$

The effect of pH on fumaric acid was inconclusive but the rate increases with increasing pH for maleic acid. Obviously the effect of pH must be studied further.

Producing sulfosuccinic acid by the maleic acid route would actually start with maleic anhydride (Keller, 1950; Cavanaugh, 1978). The cost of maleic acid is too high for use as a starting material while the anhydride is quite cheap. When maleic anhydride is added to water the hydrolysis is rapid and liberates 8.33 kcal/gmol (Encycl. of Chem. Tech., 1972). This could cause a significant temperature rise if a high concentration of maleic anhydride is used. This will be important if sulfosuccinic is produced offsite. The temperature rise can be used to decrease the reactor volume thereby decreasing capital costs.

EXPERIMENTAL METHOD AND APPARATUS

Reaction kinetics for the sulfonation of acrylic, fumaric, and maleic acids were measured in batch reactors as a function of temperature, pH, and ionic strength. Proper experimental technique required development of sampling, quenching, and analytical methods. Sulfonation with a $CaSO_3$ slurry posed special problems.

The reactor was either a beaker or flask. For low pH runs the reactor was kept sealed as much as possible to reduce SO_2 loss. SO_2 volatility increases with decreasing pH. The concentration of the acid and sulfite was chosen such that the experiment lasted two to four hours. Reaction rates were measured at room temperature (25°C) and 55°C. The heat of reaction was not large enough at the concentrations used to produce a significant temperature rise in the reaction mixture. The experiments at 55°C were done in a stirred constant temperature water bath.

The pH of the reaction mixture in all experiments was maintained at a constant value during the entire run by using a buffer. The pH range was from two to ten. High pH values were obtained with a phosphate buffer. For pH values between four and six an acetate buffer was used. The low pH values were obtained with a lactate buffer. The pH of most room temperature experiments was constantly monitored.

The ionic strength of the reaction mixture was adjusted by the use of NaCl or $MgCl_2$. Magnesium was used to model the effect of dissolved Ca^{++}. Some experiments were performed with dissolved Ca^{++} at a pH sufficiently low to avoid $CaSO_3$ precipitation. In addition to these experiments, sulfonation experiments with a $CaSO_3$ slurry were conducted to determine if sulfonation would occur.

PROCEDURE

At each reaction time a one or two ml sample was quenched by adding it to a known amount of iodine in about 10% excess of the sulfite in the sample. The time of quenching was recorded and later used to calculate the rate constant. The excess iodine was titrated with a standardized solution of sodium thiosulfate using a starch endpoint. The amount of sulfite present at the time of quenching can be calculated by the following equation:

$$[SO_3^=] = \frac{V_1M_1 - \frac{1}{2}V_2M_2}{V_s} \qquad 1\text{-}6$$

where $[SO_3^=]$ = the sulfite concentration (M)

V_1 = volume of excess iodine

M_1 = molarity of excess iodine

V_2 = volume of $Na_2S_2O_3$ used

M_2 = molarity of $Na_2S_2O_3$

V_s = sample volume

The concentration of the unsaturated acid was not followed. However, ion chromatography was used to prove there was only one reaction product. Sulfite oxidation has been suggested as a possible problem (Hagglund, 1926). Analysis of blank solutions indicates it is not a problem for this work.

As stated previously the sulfonation reaction is an irreversible second order reaction. The rate law is given by

$$\frac{d[SO_3^=]}{dt} = k[A][SO_3^=] \qquad 1\text{-}7$$

For unequal quantities of reactants the integrated rate expression is:

$$kt = \frac{1}{[A]_0 - [SO_3^=]} \ln \frac{[A][SO_3^=]_0}{[A]_0[SO_3^=]} \qquad 1\text{-}8$$

and for equimolar quantities the integrated rate expression is:

$$kt = \frac{1}{[SO_3^=]} - \frac{1}{[SO_3^=]_o} \qquad 1\text{-}9$$

or

$$kt = \frac{1}{[A]} - \frac{1}{[A]_o} \qquad 1\text{-}10$$

where k = the rate constant ($M^{-1}sec^{-1}$)

$[SO_3^=]$ = sulfite concentration (M)

$[A]$ = acid concentration (M)

o - denotes initial concentration

t = time

Experiments with unequal concentrations require knowing only the sulfite concentration if initial concentrations are known. The acid concentration can be calculated by $[A] = [A]_o - [SO_3^=]$ at time t. The rate constant can be calculated from the first expression by plotting ln $[A][SO_3^=]_o/[A]_o[SO_3^=]$ versus t. The rate constant is equal to the slope of the curve divided by $[A] - [SO_3^=]$. For equal reactant concentrations, Eq. 1-10 can be used. The inverse of the sulfite concentration is plotted against time. The rate constant is equal to the slope of the curve.

An example of equal acrylic acid and the sodium sulfite concentrations is given in Figure 1-3. This experiment was done at 55°C and pH 4.35. An acetic acid/acetate buffer was used to maintain a constant pH. NaCl was used to obtain a high ionic strength. The degree of conversion for this experiment is 75%. This is typical for most sulfonation experiments though some were

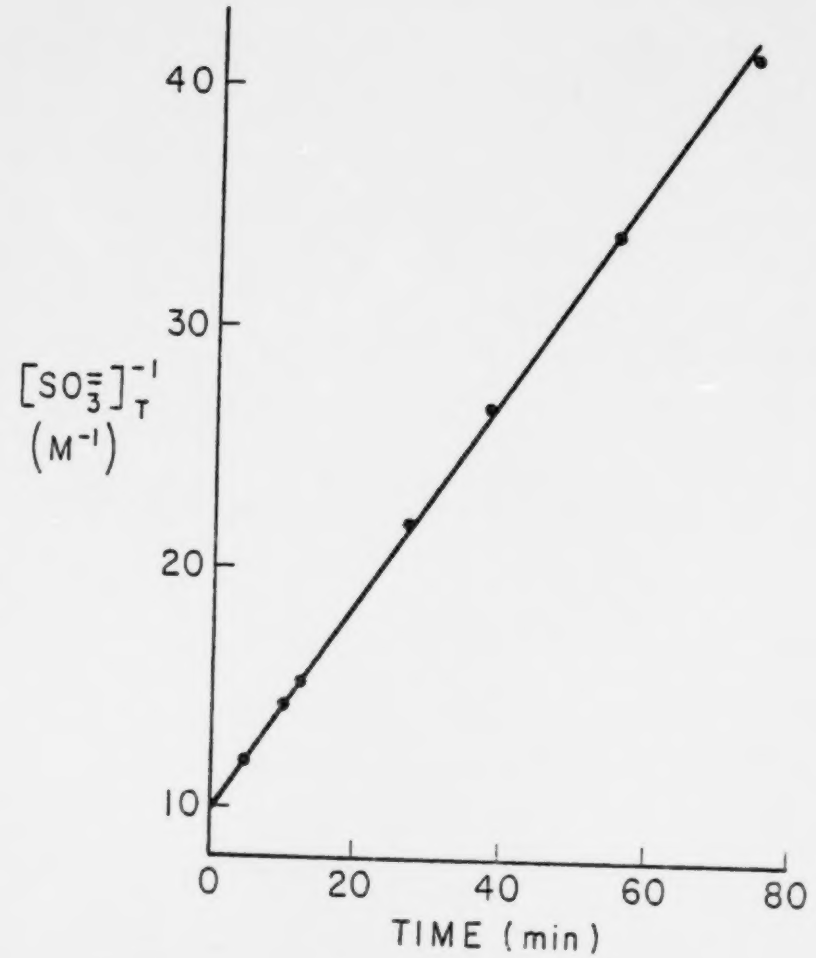


Figure 1-3: Sulfonation of acrylic acid, 55°C, pH 4.4, 0.100 M $SO_3^=$, 0.100 AA, 3.2 M Na^+, 0.5 M NaAc, 0.25 M HAc

carried almost to completion. These long experiments indicated the reaction was still second order at low concentrations. Figures 1-4 and 1-5 show similar experiments for fumaric and maleic acids. These data also indicate that the sulfonation of these acids is second order.

Analysis of experiments using a $CaSO_3$ slurry was done like previous experiments. A sample of the slurry was filtered and the dissolved sulfite determined. The rate constant was then calculated. Also, the concentration of the sulfonic acid was followed using ion chromatography. Obtaining uniform samples of a slurry are difficult and therefore the calculated rate constant is not very accurate.

The other work done with sulfonation rates was with maleic anhydride. The objective was not to measure sulfonation rate constants but instead to develop "recipes" for the offsite production of sulfosuccinic acid from maleic anhydride. Solutions containing excess maleic anhydride and $CaSO_3$ solids were prepared at room temperature. The time was noted for complete dissolution of the solids. The solutions were analyzed for total sulfite. Additional work was done using Na_2SO_3 instead of $CaSO_3$. The temperature rise of the solution was recorded and then cooled to determine if any crystallization would occur.

DISCUSSION OF RESULTS

Extensive experiments were performed with acrylic, fumaric, and maleic acids to give sulfonation rate as a function of temperature, pH, and ionic strength. These results are used later to develop process concepts. Experiments were performed with maleic anhydride to develop "recipes" for offsite production of sulfosuccinic acid.

ACRYLIC ACID

The results of sulfonation experiments of acrylic acid to sulfopropionic acid are listed in Table 1-2. As expected, the rate constant increases with increasing temperature giving an activation energy of 14 kcal/gmol. The values used for this calculation were an average of the low temperature work and the run at 55°C and pH 4.9.

A comparison of acrylic acid to some nitriles and esters is shown below (Morton and Landfield, 1952):

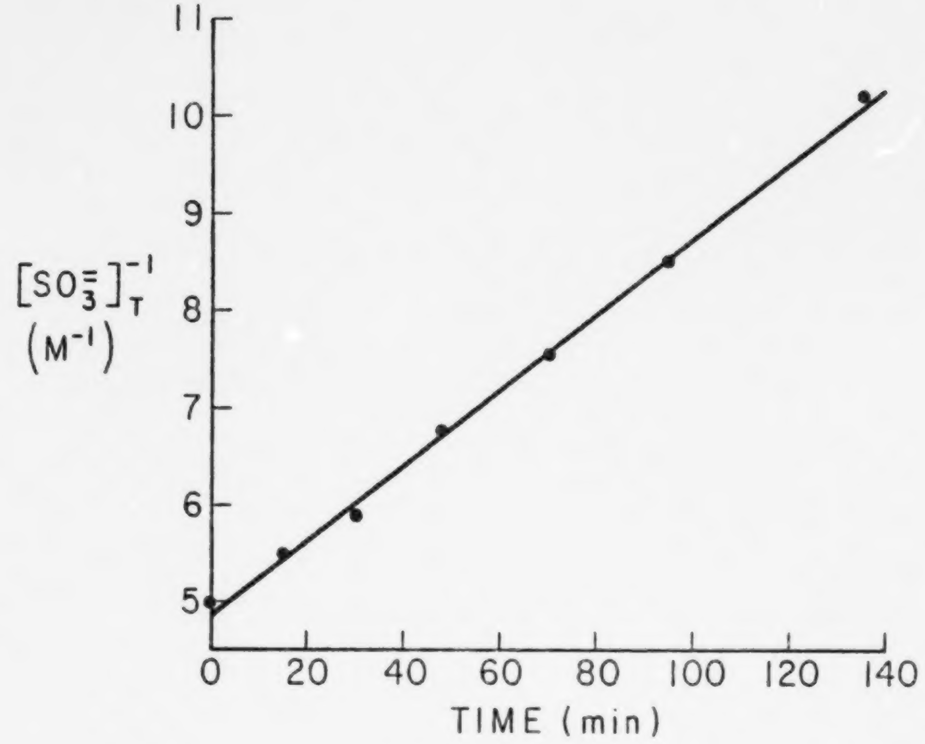


Figure 1-4: Sulfonation of fumaric acid, 55°C, pH 6.1, 0.200 M $SO_3^{=}$, 0.200 M FA, 1.3 M Na^+, 0.25 M Na_2HPO_4, 0.25 M NaH_2PO_4

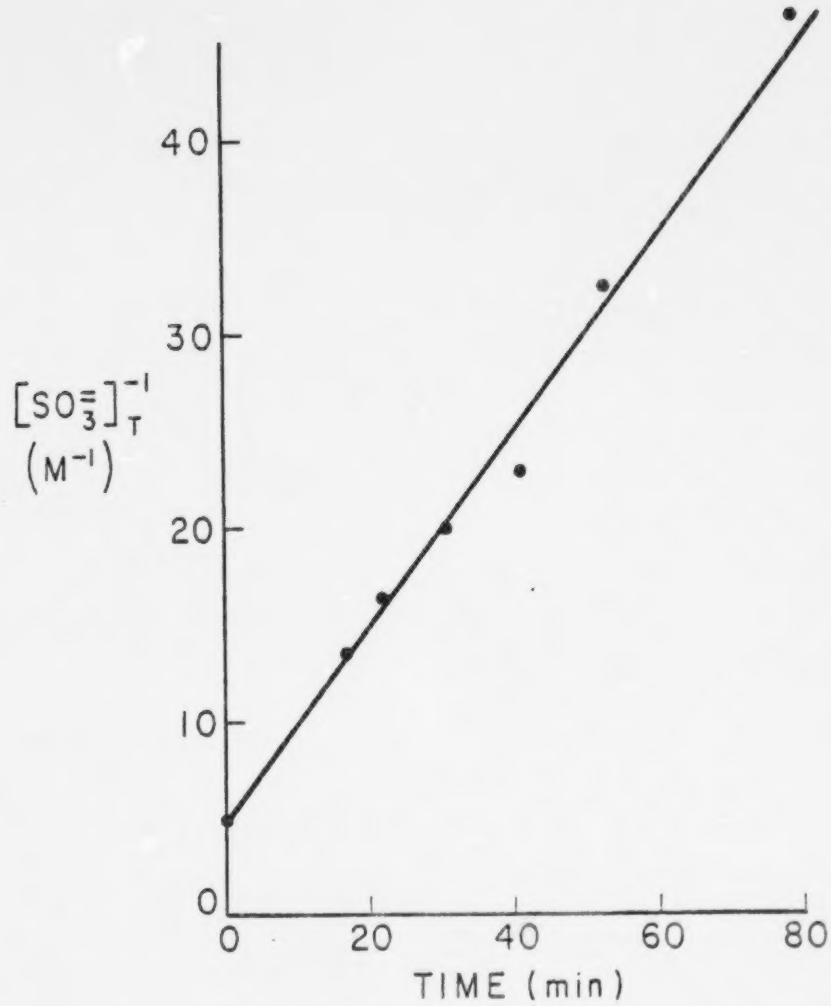


Figure 1-5: Sulfonation of maleic acid, 55°C, pH 4.6, 0.200 M $SO_3^=$, 0.200 M MA, 1.1 M Na^+, 0.5 M NaAc, 0.25 M HAc

Table 1-2: Sulfonation rates of acrylic acid

T(°C)	pH	$[Na^+]_T$(M)	I	k($M^{-1}min^{-1}$)
25	4.2	0.90	0.45	0.020
24	4.8	0.70	0.35	0.022
24	4.8	0.80	0.40	0.021
25	4.9	0.80	0.45	0.025
26	4.9	0.90	0.45	0.027
55	3.3	0.10[a]	1.05	0.21
55	3.6	0.70	0.35	0.21
55	4.3	3.20	1.60	0.43
55	4.3	0.20[b]	2.10	0.46
55	4.9	0.70	0.35	0.20
55	6.8	0.95	0.47	0.20

---

[a] plus 0.50 M Ca^{++}

[b] plus 1.0 M Mg^{++}

Compound	k at 25°C ($M^{-1}min^{-1}$)	E_a (kcal/gmol)
acrylic	0.021	14
acrylonitrile	0.0024	18.0
methyl acrylate	0.0055	12.7
methacrylonitrile	$5.8\text{x}10^{-6}$	16.2
methylmethacrylate	$3.0\text{x}10^{-5}$	12.4

The energy of activation for acrylic acid sulfonation is reasonable but the rate of sulfonation is much higher than the sulfonation of the nitriles or esters. Hagglund (1926) obtained a rate constant of 0.76 to 0.29 $M^{-1}min^{-1}$ at 80°C. Based on our measured data, the estimated rate constant at 80°C is 0.96 $M^{-1}min^{-1}$.

The effect of pH can be seen at the low and high temperatures. The pH range in the low temperature experiments is small but over this range the rate constant is independent of pH. The sulfonation experiments at 55°C indicate the rate constant is independent of pH over a wide range (3.6-6.8). This is in agreement with the results by Schenck and Danishefsky (1951). Similar experiments at pH values of 1 and 12 gave no reaction as expected (Schenck and Danishefsky, 1951). The experiment with Ca^{++} has a lower rate constant than expected. This is probably due to the low pH.

The ionic strength of the solution has a large effect on the rate constant. The salt effect equation (2-3) can be used with just the cationic strength (Rochelle, 1977). Using the tenth entry in Table 2, k_o may be calculated and the equation becomes

$$\log k = 2 \frac{(I)^{\frac{1}{2}}}{1 + (I)^{\frac{1}{2}}} - 1.44 \qquad 1\text{-}11$$

For an ionic strength of 1.6 the equation predicts a value of 0.48 $M^{-1}min^{-1}$ which is 12% higher than the experimental value of 0.43. The equation predicts a value of 0.55 $M^{-1}min^{-1}$ for the Mg^{++} experiment (I = 2.1 N) which is 20% too high.

There are two possible reasons the predictions are high. The first is that the equation was developed for ionic strengths less than 0.1 N which is much lower than the experimental conditions. The second problem lies with the expression, $Z_p^2 - Z_p^2$. The above equation was based on the reaction of acrylate and bisulfite. If any sulfite is present, then $Z_p^2 - Z_r^2$ decreases and the predicted value decreases.

The data for the Mg^{++} experiment does not suggest a strong complexing effect between Mg^{++} and acrylic acid but instead the increase in the rate constant is due mainly to the ionic strength. For the Ca^{++} experiment the calculated value is 0.36 $M^{-1}min^{-1}$ which is significantly greater than the experimental value. As stated previously this reflects the effect of low pH.

A sulfonation experiment with 0.5 M acrylic acid and 0.2 M $CaSO_3$ slurry was conducted at 25°C. The pH was maintained at 4.7 with a 0.5 M NaAc, 0.25 M HAc buffer. The total dissolved sulfite concentration was found to be 8 mM. The rate constant was 0.035 $M^{-1}min^{-1}$. This is a rough estimate because the slurry is difficult to sample uniformly.

FUMARIC ACID

The sulfonation results for fumaric acid to produce sulfosuccinic acid are listed in Table 1-3. The result at 25°C and the first result at 55°C can be used to calculate an activation energy of 6.1 kcal/gmol. This is considerably less than the 14 kcal/gmol for acrylic acid.

At 25°C Zanden (1927) measured a sulfonation rate constant of 0.0019 $M^{-1}min^{-1}$ at pH 3-5 which is considerably less than our experimental values. Zanden's data are erratic with respect to pH which suggests experimental problems. Hagglund (1926) measured a value of 0.086 $M^{-1}min^{-1}$ at 80°C. Using the above activation energy, k is predicted to be 0.062 $M^{-1}min^{-1}$.

The sulfonation rate constant is independent of pH over the range of 4.3 to 7.1. At pH 13 there is no reaction. Apparently like acrylic acid, the sulfonation does not occur between the salt and sulfite but must be between sulfite and partially associated acid.

The increase in the rate constant caused by the addition of Mg^{++} indicates the ionic environment is important. Fumaric acid shows a larger increase than acrylic acid. The fumarate-Mg^{++} ion pair is more stable than the acrylate-Mg^{++} ion pair. This provides a more stable intermediate during the sulfonation reaction.

MALEIC ACID

The results for maleic acid sulfonation are listed in Table 1-4. The energy of activation is 17 kcal/gmol based on the first two rate constants in

Table 1-3: Sulfonation rates of fumaric acid

T(°C)	pH	$[Na^+]_T$(M)	I	k($M^{-1}min^{-1}$)
25	5.4	1.24	0.45	0.012
55	4.3	0.98	0.49	0.033
55	4.7	1.26	0.63	0.031
55	4.9	0.40[a]	1.0	0.11
55	6.1	1.32	0.66	0.38
55	7.1	1.25	0.62	0.031
55	12.9	1.21	0.60	NR

---

[a] plus 0.40 M Mg^{++}

Table 1-4: Sulfonation rates of maleic acid

T(°C)	pH	$[Na^+]_T$(M)	I	k($M^{-1}min^{-1}$)
25	4.7	0.90	0.45	0.035
55	3.3	0.10[a]	1.05	0.31
55	4.6	1.08	0.54	0.52
55	5.1	0.20[b]	0.90	0.97

---

[a] plus 0.5 M Ca^{++}

[b] plus 0.4 M Mg^{++}

the table. The activation energy is about the same as for acrylic acid but much larger than for fumaric acid. The intermediate species of acrylic acid and maleic acid are much more reactive than the fumarate intermediate.

The literature data available lists rate constants at pH 5 of 0.0040 $M^{-1}min^{-1}$ at 25°C (Zanden, 1926) and 0.16 $M^{-1}min^{-1}$ at 80°C (Hagglund, 1927). Based on an activation energy of 17 kcal/gmol, the estimated rate constant at 80°C is 3.5 $M^{-1}min^{-1}$. If the ionic strengths of the two experiments are very different, this could account for the large difference.

The third entry in Table 1-4 shows the effect of ionic strength is the same as for fumaric acid. The experiment with Ca^{++} has a lower rate constant than expected. This is probably due to the low pH.

MALEIC ANHYDRIDE

Maleic anhydride undergoes rapid hydrolysis to maleic acid when placed in water. The heat of reaction is large, -8.33 kcal/gmol (Encycl. of Chem. Tech., 1972). Maleic anhydride could be used to produce sulfosuccinic acid by either in situ sulfonation or offsite production. The magnitude of the sulfonation rate constant would determine whether in situ sulfonation would be feasible.

Different considerations would be important for offsite production of sulfosuccinic acid. These would be temperature rise of the reaction mixture due to the heats of reaction and hydrolysis of maleic anhydride and solubility limits of the product salt. Sulfonation can be done with either $CaSO_3$ slurry or Na_2SO_3.

Sulfonation experiments with $CaSO_3$ slurry indicate the reaction is rapid. Experiments with $CaSO_3$ slurry were conducted with 110%, 40%, and 10% excess maleic anhydride. In all three experiments the initial maleic anhydride concentration was 1.0 M. Analysis by iodiometric titration and ion chromatography indicated all reactions went to completion in less than one hour. No solids were present, therefore the solubility of calcium sulfosuccinate is greater than 1 M. These results also indicate reaction with a $CaSO_3$ slurry is possible and using the rate constant for maleic acid with Ca^{++} in solution, process concepts can be developed for the production of sulfosuccinic acid.

The other offsite production method is to use Na_2SO_3. Several experiments with different maleic anhydride and Na_2SO_3 concentrations yielded the following "recipe;" added in the following order, 3.3 gmol of Na_2SO_3 and 3.0 gmol maleic anhydride to one liter of water. The temperature rises to approximately 80°C and all the solids are gone within one minute. The high temperature provides rapid sulfonation but should not create design problems. The sodium sulfosuccinate does not precipitate after cooling to 6°C. This could be important if shipment is required.

PROCESS CONCEPTS

The sulfonic acids can be produced by either of two methods, 1) in situ sulfonation, and 2) offsite production. In situ sulfonation is attractive because no sulfonation materials must be purchased. The unsaturated acid is added to the scrubber system where it may sulfonate. Offsite production would be used if in situ sulfonation is not feasible. This method would require the capital expense of a reactor.

IN SITU SULFONATION

The only expenses required for in situ sulfonation are material and handling costs. For in situ sulfonation to be feasible three requirements must be met. These are 1) adequate scrubber residence time for conversion to the sulfonic acid, 2) little degradation of the unsaturated acid in the system, and 3) low volatility of the unsaturated acid. The first requirement is the most important. To determine the residence time for 90% conversion, the scrubber system will be modeled as a single completely stirred tank reactor (CSTR) at pH 5 and 55°C with an average sulfite concentration of 10 mM. The residence time will depend on the sulfonation rate constant. The residence times needed for acrylic, fumaric, and maleic acids are listed in Table 1-5. The degree of conversion for the unsaturated acid in a typical scrubber with a residence time of 130 hr is also listed in Table 1-5.

Obviously 90% conversion of fumaric acid is not possible. The required sulfosuccinic acid concentration can be achieved by using a higher initial fumaric acid concentration. An alternate and cheaper method would be to use a combination of fumaric and sulfosuccinic acids to achieve the desired buffering effect. This requires knowledge of the effectiveness of fumaric acid. If degradation is not significant then a large excess of fumaric acid will not be necessary.

Table 1-5: *In situ* sulfonation of unsaturated acid

Acid	Residence time (hr)	% conversion
acrylic	71	94
fumaric	480	71
maleic	48	96

Table 1-6: Reactor volumes and residence times for unsaturated acid sulfonation by $CaSO_3$ and Na_2SO_3 at 25°C

Acid	acrylic	fumaric	maleic
1 M $CaSO_3$			
Batch			
vol (ft^3)	2,640	3,120	1,070
t (hr)	166	312	111
CSTR			
vol (ft^3)	10,300	12,200	4,170
t (hr)	652	950	429
3 M Na_2SO_3			
Batch			
vol (ft^3)	93	442	38
t (hr)	5.9	22.7	3.9
CSTR			
vol (ft^3)	940	2200	380
t (hr)	59	114	39
3 M Na_2SO_3, 80°C			
CSTR			
vol (ft^3)	2.5	24	0.4
t (min)	28	440	7.8

OFFSITE PRODUCTION

Sulfonation can also be accomplished offsite by using $CaSO_3$ slurry or Na_2SO_3 at the power plant site or Na_2SO_3 at the supplier's plant. Offsite production would be used to avoid unsaturated acid degradation.

Two different reactor types can be used to produce the sulfonic acid, a completely stirred tank reactor (CSTR) or a batch reactor. A CSTR would have a larger volume than a batch reactor and would require storage tanks for the reactants. The advantages of a CSTR are lower material and labor handling costs and easier automatic control. With batch operation two reactors would be used. One reactor would be used for sulfonation while the other is being emptied into the scrubber system. The reactors would be rotated over a given period of time. Total reactor volume would be less than the CSTR but would require operator attention.

The concentration of the product would depend on either the $CaSO_3$ or the salt solubility limit. The slurry contains 1.2 M $CaSO_3$ and this would set the product concentration if $CaSO_3$ was used for sulfonation. If Na_2SO_3 was used as the sulfonating agent then the product concentration would be determined by the solubility of the salt which is approximately 3 M. Some additional precautions must be taken with fumaric and acrylic acids. Fumaric acid has a low solubility (0.1 M) and to obtain a high concentration an equimolar amount of NaOH must be added. Care must be taken to avoid high temperature and concentrations with acrylic acid because these conditions promote polymerization. This is important because polyacrylic acid has been shown to inhibit $CaCO_3$ dissolution (Chan, 1981).

The process concepts which will be discussed are based on the following plant specifications:

500 MW unit
50% solids in the waste ($CaSO_3$ 1/2H_2O)
3% sulfur in the coal
90% SO_2 removal
no acid degradation in the system

The required makeup rates to get 20.6 mM sulfopropionic and 12.2 mM sulfosuccinic acids are respectively, 1.1 and 0.67 lbmol/hr. Preliminary economic optimization suggests ambient temperature is the most cost effective. The heat of sulfonation for acrylic and maleic anhydride at high concentrations (3M) can be taken advantage of in CSTR operation. Operating temperature in a CSTR would be approximately 80°C.

Table 1-6 lists volumes and residence times for batch reactors and CSTR's at 25°C using either $CaSO_3$ or Na_2SO_3. Also listed are volumes and residence times for Na_2SO_3 sulfonation at 80°C. The heat of sulfonation (plus heat of hydrolysis of maleic anhydride) allows adiabatic operation above 70°C for a CSTR using Na_2SO_3.

Another production method which takes advantage of the heat of reaction are "recipes" developed for the production of sulfosuccinic acid from maleic anhydride. The following "recipe" provides a useful basis for a production scheme of sulfosuccinic acid from maleic anhydride:

3.3 gmol of Na_2SO_3 (10% excess)
3.0 gmol of maleic anhydride
1 liter of water

The reaction mixture temperature will rise to approximately 80°C and can be cooled to at least 6°C without any precipitation. For the above mixture, 95% conversion will take less than two minutes. A similar scheme could be developed for acrylic acid. Fumaric acid would not have as large a temperature rise.

The method of acrylic acid sulfonation would depend on whether it was done at the power plant or not. Production at the power plant could be done in a CSTR or batch reactor. A supplier would probably choose a CSTR. Fumaric acid would only be used at the power plant location because it is not a health hazard. Due to the high cost of fumaric acid a supplier would prefer maleic anhydride and take the necessary material handling precautions. The "recipe" described above would work well for sulfosuccinic acid production. The supplier would add all the reactants to a tank car full of water which would then be shipped immediately to the user. A typical tank car with a capacity of 20,000 gal would last two months. A similar production method could be used for acrylic acid. If this production method is not suitable for the contractor, a CSTR would be used for production.

CHAPTER 1-3

HYDRATION OF ACRYLIC ACID

INTRODUCTION

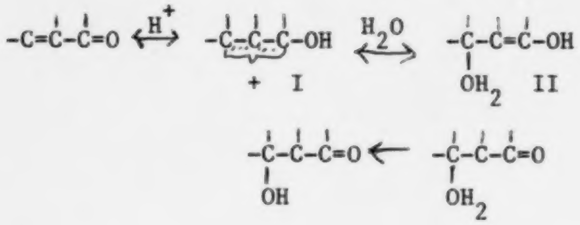
A solution with a concentration of 15 mM hydroxypropionic acid has been shown to enhance SO_2 absorption (Weems, 1980) and therefore could be attractive for use as an organic buffer for FGD throwaway scrubbing systems. Also, hydroxypropionic acid and its degradation products should be nonvolatile under scrubber conditions due to the hydroxy group. Hydroxypropionic acid is probably a sulfite oxidation inhibitor which may be useful in the scrubber system (Hudson, 1979; Rochelle, 1980). Because it inhibits sulfite oxidation, its degradation rate is generally less than that of adipic acid (Rochelle, Nov. 1980).

Before the use of hydroxypropionic acid can be considered further an economical production method must be developed. Hydration of acrylic acid requires acid catalysis and high temperatures (100°C). Sulfuric acid is the logical choice for the catalyst because of the low cost. Caution must be taken to minimize acrylic acid polymerization by using an adequate amount of acid catalyst.

It may be possible to hydrate acrylic acid in the presence of a H^+ loaded sulfonated polystyrene resin. A plug flow reactor (PFR) would be the best choice for this method. Possible limitations might be the maximum operating temperature of the resin, small reaction rate constant, and a large pressure drop through the reactor. This method may be attractive because it eliminates the need to handle sulfuric acid.

LITERATURE REVIEW

The hydration of unsaturated compounds is acid catalyzed. The reaction is an electrophilic addition and takes place in such a way as to form the most stable intermediate carbonium ion. Addition to α,β-unsaturated carbonyl compounds occurs by the following mechanism (Hall, 1950; Morrison and Boyd, 1973):



Intermediate I is the more stable carbonium ion because the positive charge is carried by carbon and not the electronegative oxygen. Attack at an position by the electrophile does not form as stable an intermediate. Therefore attack must be at the β position.

The acid catalyzed hydration of acrolein (Hall and Stern, 1950) and acrolein and acrylic acid (Pressman and Lucas, 1942) has been studied. The forward and reverse reactions are second order overall, first order in H^+ and in aldehyde or acid. For a constant H^+ concentration the rate expression can be written as first order. The rate expression for acrylic acid is given by the following:

$$r = k_f[AA] - k_r[HP] \tag{1-12}$$

where $[AA]$ = acrylic acid concentration (M)

$[HP]$ = hydroxypropionic acid concentration (M)

k_f = rate constant for forward reaction (hr^{-1})

k_r = rate constant for reverse reaction (hr^{-1})

Pressman and Lucas (1942) measured k_f for a solution with an ionic strength of 2.00 N and obtained 0.159 hr^{-1} at 110.6°C and 0.296 hr^{-1} at 119.8°C with an activation energy of 20.3 kcal/gmol. The initial concentration of acrylic acid ranged from 0.03 M to 0.05 M and $HClO_4$ was used as a catalyst.

There are two inadequacies with the literature data. The acrylic acid concentration is too low since a production method would use a concentration from 1 to 2 M acrylic acid. However, at high concentrations acrylic acid polymerizes. Therefore, a production method must be devised to minimize this problem. Hydration must also be investigated using a cheaper acid such as H_2SO_4 instead of $HClO_4$.

The previous production method for hydroxypropionic acid using 1 M acrylic acid made no attempt to measure the rate constant (Cavanaugh, 1978). The acid was produced at 100 and 106°C. A 1 M acrylic acid and 2 M H_2SO_4 solution was used. Reaction times at 106°C were 20.5 and 68.5 hr and at 100°C the reaction time was 12 hr. Equilibrium concentrations were not determined.

EXPERIMENTAL METHOD AND APPARATUS

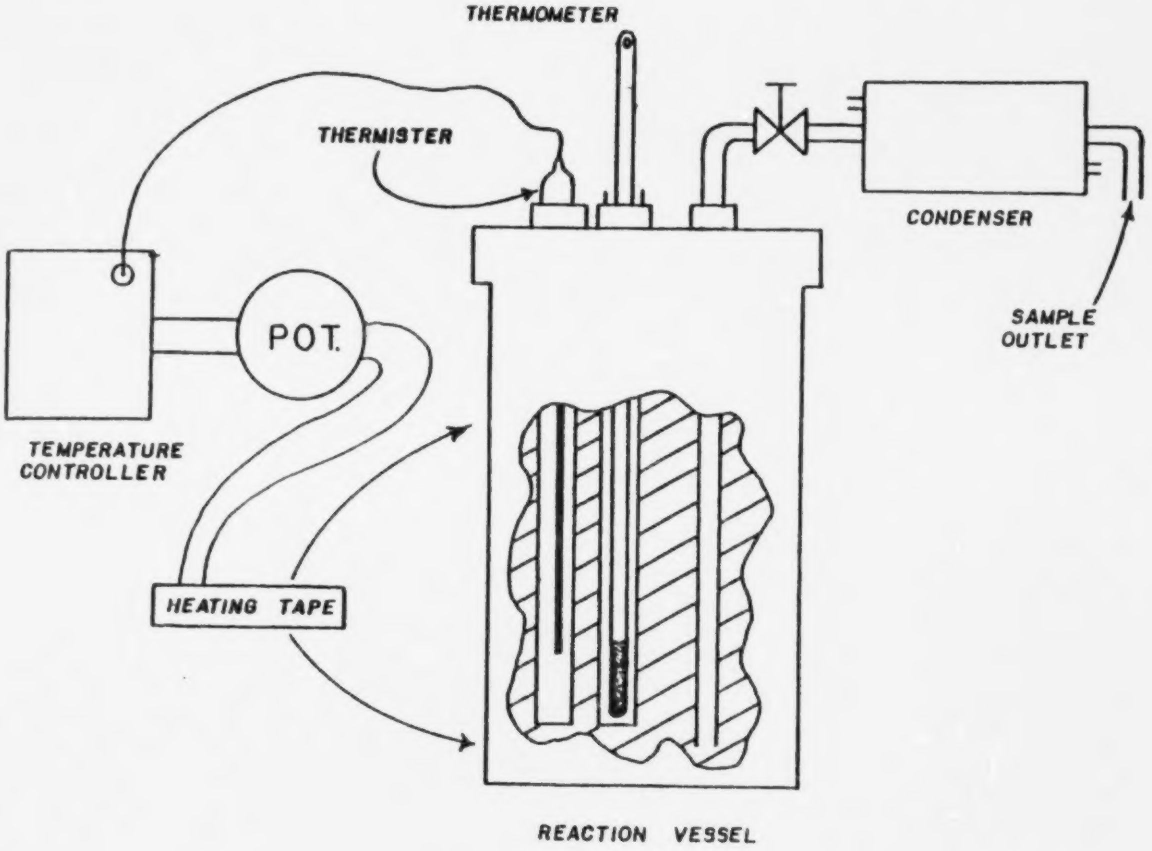
Reaction kinetics for the hydration of acrylic acid were measured in batch reactors as a function of temperature and pH. An analytical method was developed to sample, quench, and analyze the sample by ion exclusion chromatography. Three different hydration methods were employed.

Two different reactors were used (Figures 1-6 and 1-7). The apparatus in Figure 1-6 is a modified "bomb" calorimeter. The reactor was heated with electrical resistance tape powered by a variac. The variac was controlled by a temperature controller which maintained a constant temperature within ±2°C. A thermistor in the temperature well was used to monitor the temperature. The temperature range in which the calorimeter was operated was 100 to 140°C. The sample was taken by opening the valve on the sample tube. A condenser on the tube cooled the sample. The sample tube and temperature well were constructed of Teflon because of the corrosive nature of the hot H_2SO_4-acrylic acid solution. The "bomb" contained approximately 300 ml of solution.

The second apparatus used in shown in Figure 1-7. It consisted of a three-necked round-bottom flask fitted with a reflux condenser. Temperature was monitored with a thermometer in one of the side necks. The reactor was heated with a heating jacket. The temperature of the reactor was 100±0.1°C. This reactor provided much better temperature control. The amount of vapor lost through the side of the reflux condenser was negligible.

The third method of hydrating acrylic acid was the second reactor. Instead of using H_2SO_4 as a catalyst, a H^+ loaded sulfonated polystyrene resin was used. The resin was Dowex 50W-X4 with a total exchange capacity of 1.3 meg/ml (wet basis), 67% moisture content, and a maximum operating temperature of 140°C. The H^+ concentration was estimated at 0.4 M. The resin was kept agitated with a magnetic stirrer. Prior to sample analysis, the sample was filtered to remove any resin.

Figure 1-6: "Bomb" calorimeter for acrylic acid hydration


THERMOMETER
THERMISTER
CONDENSER
SAMPLE OUTLET
TEMPERATURE CONTROLLER
POT.
HEATING TAPE
REACTION VESSEL

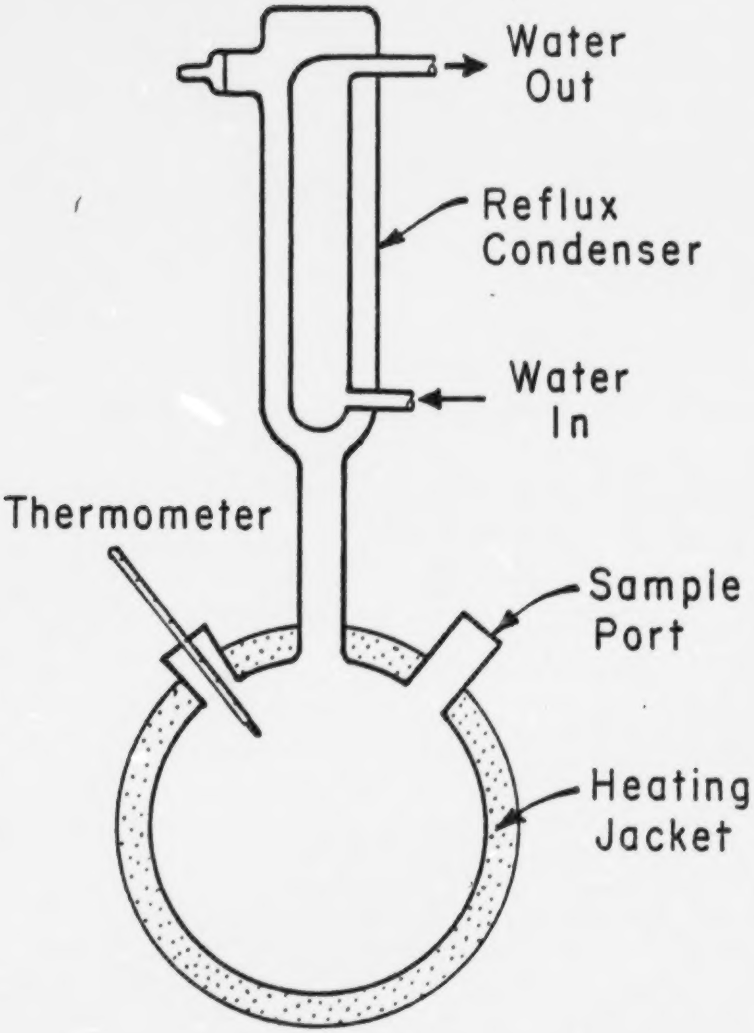

Water
Out
Reflux
Condenser
Water
In
Thermometer
Sample
Port
Heating
Jacket

Figure 1-7: Stirred batch reactor for acrylic acid hydration

PROCEDURE

Two methods were used to analyze for acrylic acid. The first method, which was used on only one experiment, was bromine titration (see Appendix F). The second method used ion exclusion chromatography (ICE). No determination of the hydroxypropionic acid concentration was done because no standard existed for comparison, however, the hydration product was observed as a peak in ICE analysis.

Once the acrylic and hydroxypropionic acid concentrations were known as a function of time the hydration rate constant could be calculated. For a reversible reaction the rate expression is written as:

$$\frac{d[AA]}{dt} = -k_f[AA] + k_r[HP] \qquad 1\text{-}13$$

where $[AA]$ = acrylic acid concentration (M)

$[HP]$ = hydroxypropionic acid concentration (M)

k_f = forward rate constant (min^{-1})

k_f = reverse rate constant (min^{-1})

t = time (min)

Knowing $[HP] = [AA]_o - [AA]$ and $k_f[AA]_{eq} = k_r([AA]_o - [AA]_{eq})$ where o denotes initial concentration and eq is equilibrium, the rate expression can be written as

$$\frac{d[AA]}{dt} = \frac{k_r[AA]}{[AA]_{eq}}([AA]_0 - [AA]) \qquad 1\text{-}14$$

Integrating the above gives:

$$\ln\frac{[AA]_{eq} - [AA]_0}{[AA]_{eq} - [AA]} = \frac{k_r[AA]_0}{[AA]_{eq}}t = (k_f + k_r)t \qquad 1\text{-}15$$

A plot of $-\ln([AA]_{eq} - [AA])$ versus t gives a slope equal to $k_f + k_r$. Note the above equations are for a first order reaction. The H^+ concentration remains constant, therefore the hydration reaction can be written as a first order reversible reaction. The equilibrium rate constant, K, is calculated from k_f/k_r.

A typical set of data is shown in Figure 1-8. The data shows that the forward and reverse reactions are first order with respect to the acid.

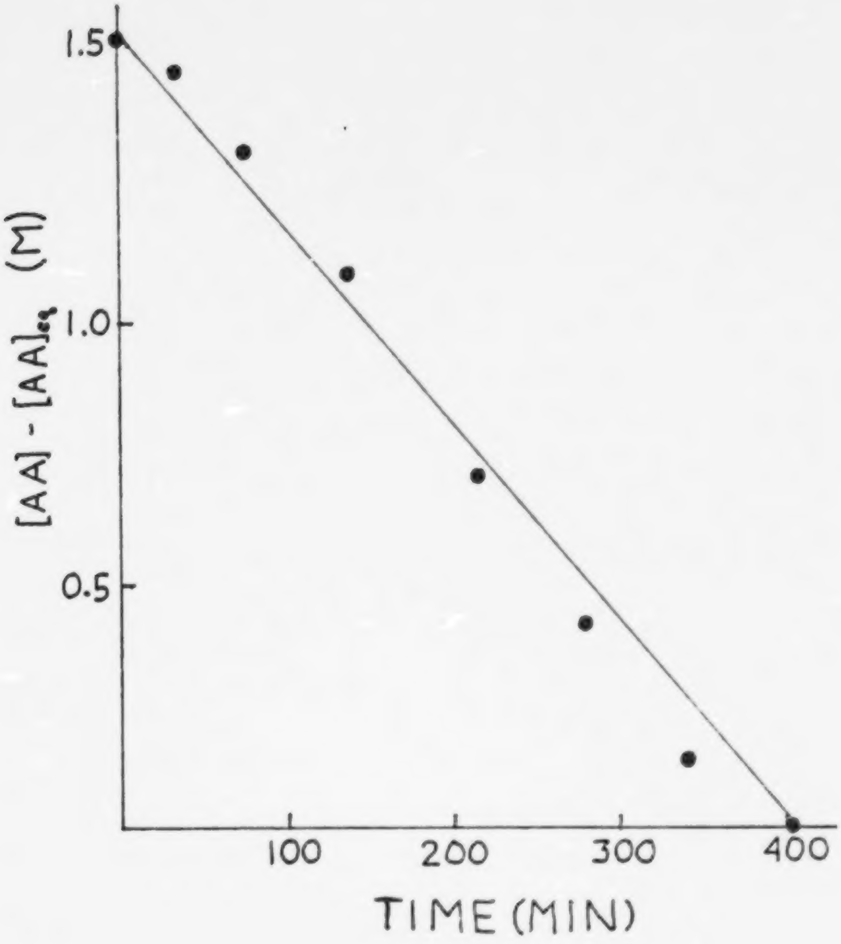


Figure 1-8: Acrylic acid hydration, 2.0 M AA, 1.0 M $_2SO_4$, 100°C

Hydration experiments lasted seven to thirty hours. The long reaction times were necessary to obtain an accurate value for the equilibrium concentrations. Conversion of hydroxypropionic acid was always greater than 90%.

DISCUSSION OF RESULTS

Several hydration experiments were conducted to determine the rate as a function of temperature and catalyst concentration. One experiment was done to hydrate acrylic acid with a H^+ loaded resin. The hydration results are given in Table 1-7 and Figure 1-9. The second-order rate constant is given by $k = 1.14 \times 10^9 \exp[-17{,}000/RT)$.

Some results obtained by Pressman and Lucas (1942) are shown below:

T(°C)	k_f/H_3O^+	k_r/H_3O^+	K
110.6	0.159	0.0142	11.3
119.8	0.296	0.0321	9.27
134.7			6.79

K is the equilibrium constant defined by either [HP]/[AA] or k_f/k_r. From the above data it can be seen that $k_f >> k_r$. Therefore, a measure of the rate constant will essentially be a calculation of k_f.

Analysis of our data shows that equilibrium was not reached and therefore k_f and k_r cannot be separated. A good estimate, however, can be made for k_f because $k_f + k_r = k_f$. The rate obtained at 120°C is 0.38 $M^{-1}hr^{-1}$ which is higher than that obtained by Pressman and Lucas. This suggests that sulfuric acid may have specific interactions with either reactants or products, such as ester formation.

Figure 1-9 gives the measured hydration rate constant as a function of temperature. The estimated activation energy is 17 kcal/gmol. Pressman and Lucas (1942) obtained 20.4 kcal/gmol.

The experiment with the resin indicates it can hydrate acrylic acid. The value of $(k_f + k_r)/[H_2SO_4]$ was calculated using an estimated value of H^+ concentration. The H^+ concentration was based on the total milliequivalents of H^+ of the resin and the volume of the solution. The resin works as well as sulfuric acid.

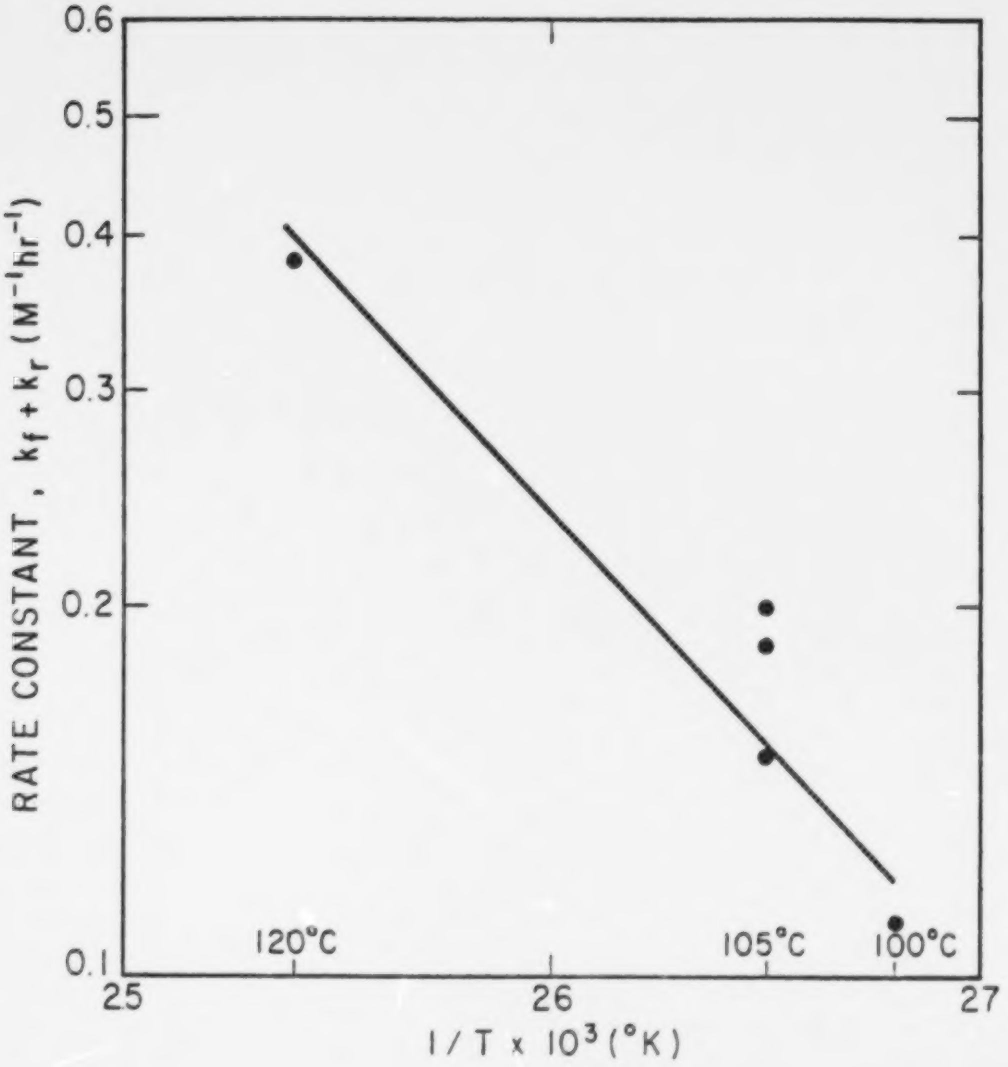


Figure 1-9: Energy of activation for acrylic acid hydration

Table 1-7: Hydration of acrylic acid

T(°C)	[AA] (M)	H_2SO_4 (M)	[a]$(k_f + k_r)/[H_2SO_4]$
55	2.0	1.5	NR
100	2.0	1.0	0.11
100	2.0	resin	0.11
105	2.0	1.5	0.20
105	2.0	0.5	0.15
105	4.0	0.5	[b]0.26
105	2.0	0.1	0.18
105	2.0	0	NR
120	1.9	1.0	0.38
140	2.0	1.5	1.6

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[a] forward + reverse rate constants ($M^{-1}hr^{-1}$)

[b] includes polymerization

Table 1-8: Reactor volumes and residence times for 85% conversion of acrylic acid to hydroxypropionic acid (1 M)

	CSTR		Batch Reaction	
T(°C)	Vol(ft^3)	t(hr)	Vol(ft^3)	t(hr)
105	1340	85	230	14
120	630	40	130	8.2

PROCESS CONCEPTS

The production of hydroxypropionic acid involves the choice of reactor type, operating temperature, and catalyst. Table 1-8 shows a comparison between batch reactors (or PFR) and CSTR's at different temperatures for 85% conversion with 1 M H_2SO_4. The acrylic acid concentration was set at 2 M as an estimated tradeoff between reactor volume land polymerization. Experiments with less than 1 M H_2SO_4 had small amounts of polymer present. Makeup rate for hydroxypropionic acid was 1.1 lbmol/hr.

The type of reactor to use would be determined by the producer. Even though capital costs are higher, a CSTR is probably the most attractive type because of the easier automatic control. The use of multiple CSTR's in series would decrease the total reactor volume required. In general equal reactor volumes are used to minimize the costs of engineering design, construction, fabrication, and inventory of spare parts. The greatest reduction in volume will occur when two reactors are used and probably for this process it would not be desirable to use more reactors. At 105°C, each reactor volume would be 260 ft^3 for a total of 520 ft^3 as compared to 1340 ft^3 for a single tank. Since the volume for one reactor is not large it seems multiple reactors are unnecessary.

The operating temperature would probably be 100°C or less to eliminate design problems for operating at high pressure. An optimization of energy and capital costs would determine the actual operating temperature. An additional benefit of operating at a lower temperature is the reduction of polyacrylic acid formation.

One additional method of hydration would use a H^+ loaded resin in a packed bed reactor. The PFR would have a low flow rate which means the reactor design would have to take into account axial and back mixing. An advantage of this production method is no H_2SO_4 or H_2SO_4 handling facilities are needed. Use of the resin would depend on the resin life under reaction conditions.

CHAPTER 1-4

CONCLUSIONS AND RECOMMENDATIONS

1. Second order rate constants ($M^{-1}min^{-1}$) for the addition of bisulfite to acrylic, fumaric, and maleic acids at ionic strength 1.2 N and pH 5 are, respectively, $k = 4.48x10^{8}exp[-14,100/RT]$, $k = 372exp[-6100/RT]$, and $k = 2.38x10^{11}exp[-17,500/RT]$.

2. Increased ionic strength and the substitution of Mg^{++} or Ca^{++} for Na^{+} give faster rates by stabilizing the reaction intermediate.

3. The second order rate constant for hydration of acrylic acid catalyzed by H_2SO_4 or H^{+} loaded ion exchange resin is $k = 1.14x10^{9}exp[-17000/RT]$.

4. _In situ_ sulfonation is feasible and attractive for acrylic acid and maleic anhydride if the unsulfonated acids are not sensitive to degradation.

5. Maleic anhydride can be effectively sulfonated by reaction with Na_2SO_3 if the power plant is unwilling to take the necessary precaution for onsite handling.

6. Fumaric acid is not attractive for sulfonation. _In situ_ sulfonation is not feasible and maleic acid is a better alternative for offsite production.

7. Hydroxypropionic acid can be produced in an offsite reactor at approximately 100°C using H_2SO_4 or H^{+} loaded resin as a catalyst.

8. Future work should focus on degradation of the unsaturated and saturated acids under scrubber conditions.

9. A simple method is needed to prevent acrylic acid polymerization or to remove polyacrylic acid during either sulfopropionic or hydroxypropionic acid production.

APPENDIX A: CHEMICAL REAGENTS

Chemical*	Formula	Purity	Source
Acetic Acid (l)	CH_3CO_2H	Glacial	Matheson Coleman & Bell
Acrylic Acid (l)	CH_2CHCO_2H	99% b.p. 139°C	Aldrich Chemical Co. Eastman
Calcium Chloride (s)	$CaCl_2$	Laboratory Grade	Fisher Scientific Co.
Calcium Hydroxide (s)	$Ca(OH)_2$	Reagent, A.C.S.	Matheson Coleman & Bell
Calcium Sulfite (s)	$CaSO_3$ - 1/2 H_2O		Synthesized
Dowex 50X2-200		1.3 meg/ml, 5.1 meg/g	Aldrich Chemical Co.
Fumaric Acid (s) Co.	$HO_2CHCHCO_2H$	Laboratory Grade	Fisher Scientific
Hydrochloric Acid (l)	HCl	Certified 1N (1.0010-0.9995N)	Fisher Scientific Co.
Hydrochloric Acid (l)	HCl	Reagent, A.C.S. 36.5 - 38.0%	Fisher Scientific Co.
Hydroxypropionic Acid (l)	$HOCH_2CH_2CO_2H$		Synthesized

Chemical*	Formula	Purity	Source
Iodine (l)	I_2	Certified 1N (1.0010-0.9995N)	Fisher Scientific Co.
Potassium Bromate (s)	$KBrO_3$	Laboratory Grade	Matheson Coleman & Bell
Potassium Bromide (s)	KBr	Certified A.C.S.	Fisher Scientific Co.
Potassium Iodide (s)	KI	Reagent, A.C.S.	Matheson Coleman & Bell
Lactic Acid (l)	$CH_3CH(OH)CO_2H$	Reagent, A.C.S. 85%	Matheson Coleman & Bell
Magnesium Acetate (s)	$Mg(CH_3CO_2)_2 \cdot 4H_2O$	Certified	Fisher Scientific Co.
Magnesium Chloride (s)	$MgCl_2 \cdot 6H_2)$	Reagent, A.C.S.	Matheson Coleman & Bell
Maleic Acid (s)	$HO_2CCHCHCO_2H$	Reagent Grade M.P. 134-139°C	Fisher Scientific Co.
Maleic Anhydride (s)	$(CHCHCO)_2O$	Certified M.P. 52.2-53.2°C	Fisher Scientific Co.
Phosphoric Acid (l)	H_3PO_4	Reagent 85%	J.T. Baker Chemical Co.
Polyacrylic Acid (l)	$[-CH_2CH(CO_2H)-]$	25% Solution Ave. M.W. 90,000	Aldrich Chemical Co.

Chemical*	Formula	Purity	Source
Sodium Acetate (s)	$NaOOCH_2$	Reagent, A.C.S.	J.T. Baker Chemical Co.
Sodium Bisulfite (s)	$NaHSO_3$	Certified A.C.S.	Fisher Scientific Co.
Sodium Chloride	$NaCl$	Certified A.C.S.	Fisher Scientific Co.
Sodium Hydroxide (s) (pellet form)	$NaOH$	Certified A.C.S. 98.3%	Fisher Scientific Co.
Sodium Hydroxide (l)	$NaOH$	Certified 1N (1.005-0.995N)	Fisher Scientific Co.
Sodium Sulfide (s)	Na_2SO_3	Analytical Reagent	Mallinckrodt
Starch (s)		Certified A.C.S.	Fisher Scientific Co.
Sulfopropionic Acid (l)	$CH_2(SO_2)CH_2CO_2H$		Synthesized
Sulfuric Acid	H_2SO_4	Reagent, A.C.S. 98%	Matheson Coleman & Bell
Sulfosuccinic Acid (l)	$HO_2CCH_2CH(SO_3)CO_2H$		Synthesized

*(l) indicates chemical in liquid form; (s) indicates chemical in solid form.

APPENDIX 1-B

SULFONATION IN A CSTR

$CaSO_3$ Sulfonation

The design equation for a constant volume system is (Hill, 1977);

$$t = \frac{C_{AO}(f_{A,out} - f_{A,in})}{-r}$$

where t = time

C_{AO} = initial concentration of limiting species

$f_{A,out}$ = final degree of conversion of A

$f_{A,in}$ = initial degree of conversion of A

r = rate expression for the reaction

The rate expression for a second-order irreversible reaction is:

$$-r = kC_A C_{BO}$$

where C_A = acid concentration

C_{BO} = total sulfite concentration

k = rate constant ($M^{-1}min^{-1}$)

Because of the low $CaSO_3$ solubility the concentration of sulfite can be assumed to be constant, therefore $C_B = C_{BO}$. The acid concentration at any time is $C_A = C_{AO}(1 - f_A)$. Making these substitutions into the rate expression gives the final equation:

$$t = \frac{f_{A,out} - f_{A,in}}{k(1-f_A)C_{BO}}$$

The reactor volume is calculated by $V_R - v_o t$ where V_R is the reactor volume land v_o is the volumetric flow rate.

Na_2SO_3 Sulfonation

The rate expression can be written in terms of initial concentrations and degree of conversion to give:

$$-r = kC_A^2(1 - f_A)(C_{BO} - f_A C_{AO})$$

Substitution of this expression into the design equation from the previous section gives:

$$t = \frac{f_{A,out} - f_{A,in}}{k(1-f_A)(C_{BO}-f_A C_{AO})}$$

and the reactor volume is calculated by $V_R = v_o t$.

APPENDIX 1-C

SULFONATION IN A BATCH REACTOR

$CaSO_3$ Sulfonation

The design equation for a batch reactor is (Hill, 1977):

$$t = C_{AO} \int_0^{f_A} \frac{df_A}{-r}$$

where t = residence time of the reactor
C_{AO} = concentration of limiting species A
$-r$ = rate of sulfonation

The rate of sulfonation is:

$$-r = kC_AC_B$$

where k = rate constant ($M^{-1}time^{-1}$)
C_A = concentration of species A
C_B = concentration of total sulfite in solution

The sulfite concentration can be assumed to be constant because of the low $CaSO_3$ solubility, therefore $C_B = C_{BO}$. The concentration of the acid is given by $C_A = C_{AO}(1 - f_A)$. Substituting the above rate expression gives:

$$t = \frac{1}{kC_{BO}} \int_0^{f_A} \frac{df_A}{1-f_A}$$

Integrating the above expression gives:

$$t = -\frac{\ln(1-f_A)}{kC_{BO}}$$

The volume of the reactor is calculated by $V_R = v_ot$ where V_R is the reactor volume and v_o is the volumetric flow rate.

Na_2SO_3 Sulfonation

The rate expression can be written as a function of the initial concentrations and degree of conversion:

$$-r = kC_{AO}(1 - f_A)(C_{BO} - C_{AO}F_A)$$

The design equation from the previous section becomes:

$$t = \frac{1}{k} \int_0^{f_A} \frac{df_A}{(1-f_A)(C_{BO}-C_{AO}f_A)}$$

Integrating yields:

$$t = \frac{1}{k(C_{BO}-C_{AO})} \ln \frac{(1-f_A)}{(C_{BO}-C_{AO}f_A)}$$

The reactor volume is calculated by $V_R = v_o t$.

APPENDIX 1-D

ACRYLIC ACID HYDRATION

CSTR

The design equation for a constant volume system is (Hill, 1977):

$$t = \frac{C_{AO}(f_{A,out} - f_{A,in})}{-r}$$

where C_{AO} = initial acrylic acid concentration
t = residence time of the CSTR
$f_{A,out}$ = final conversion of acrylic acid
$f_{A,in}$ = initial conversion of acrylic acid
$-r$ = rate of hydration

The rate for a first order reversible reaction is:

$$-r = k_f C_A - k_r C_B$$

where k_f = forward first order rate constant
k_r = reverse first order rate constant
C_B = concentration of hydroxypropionic acid

Writing in terms of initial concentrations:

$$\begin{aligned} -r &= k_f C_{AO}(1 - f_A) - k_r(C_{AO} - C_A) \\ &= k_f C_{AO}(1 - f_A) - k_r C_{AO}\ 1 - (1 - f_A) \\ &= k_f C_{AO}(1 - f_A) - k_r C_{AO} f_A \\ &= k_f C_{AO} - (k_f + k_r) C_{AO} f_A \end{aligned}$$

Substituting the last expression into the design equation gives:

$$t = \frac{f_{A,out} - f_{A,in}}{k_f - (k_f + k_r) f_{A,out}}$$

The volume is $V_R = v_o t$ where V_R is the reactor volume and v_o is the volumetric flow rate.

Multiple CSTR's

The design equations for two CSTR's are

$$t = \frac{f_{A1}}{k_f - (k_f + k_r)f_{A1}} = \frac{V_{R1}}{v_0}$$

$$t = \frac{f_{A2} - f_{A1}}{k_f - (k_f + k_r)f_{A2}} = \frac{V_{R2}}{v_0}$$

Usually for series reactors, the volumes are equal. Therefore, the volumes can be determined by letting $V_{R1} = V_{R2}$ and then:

$$\frac{f_{A1}}{k_f - (k_f + k_r)f_{A1}} = \frac{f_{A2} - f_{A1}}{k_f - (k_f + k_r)f_{A2}}$$

Once f_{A1} is determined for a given value of f_{A2}, then the reactor volumes can be calculated.

Batch Reactor

Design equation for a constant volume system is:

$$f = C_{AO} \int_0^{f_A} \frac{df_A}{-r}$$

Substituting the rate expression from the previous section gives:

$$f = \int_0^{f_A} \frac{df_A}{k_f - (k_f + k_r)f_A}$$

Integrating between limits:

$$t = -\frac{1}{k_f + k_r} [\ln(k_f - (k_f + k_r)f_A) - \ln k_f]$$

The reactor volume is calculated from $V_R = v_o t$

APPENDIX 1-E

$CaSO_3$ DISSOLUTION

Three dissolution experiments of $CaSO_3$ were conducted. The dissolution of $CaSO_3$ was compared to $CaSO_3$ dissolution with acrylic and polyacrylic acids also in solution. A solution of 0.2 M $CaCl_2$ containing 0.5 mM HSO_3^- was prepared. The pH was adjusted to 5. Enough $CaSO_3$ was added to produce a 0.01 M solution. As the pH changed, $NaIO_3$ was added to keep the pH constant. The rate of $NaIO_3$ addition was equal to the rate of $CaSO_3$ dissolution. The stoichiometry of the reaction is given by the following equation:

$$3CaSO_3 + NaIO_3 \longrightarrow 3CaSO_3 + NaI$$

The results are shown in Figure 1-10. Obviously, acrylic and polyacrylic acids increase the dissolution rate significantly. The rate is about seven times faster with polyacrylic or acrylic acid.

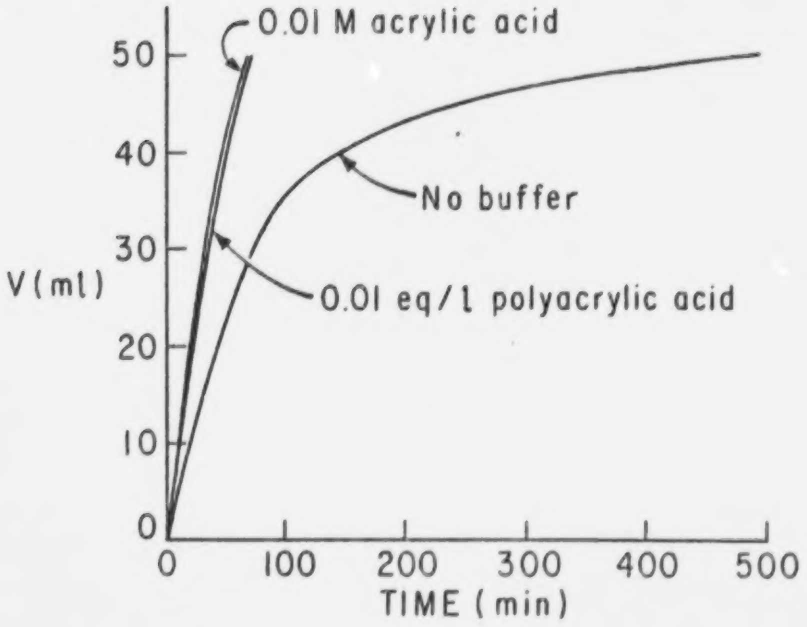

Figure 1-10: Dissolution of $CaSO_3$ in the presence of polyacrylic and acrylic acids

APPENDIX 1-F

BROMINATION METHOD

The bromine method was used only once because this technique is difficult and time consuming. The following procedure was used (Siggia, 1954; Chemical Analysis, Vol. 32, 1970) for an experiment with an initial acrylic acid concentration of 2.0 M at 120°C. Five ml samples were taken from the reaction vessel every two hours and added to an evacuated bromination bottle. This was followed by 5 to 10 ml of distilled water and 25 ml of 0.1 N BrO_3^-/Br^- reagent. The bottle was then cooled in an ice bath. After cooling, 25 ml of 10% H_2SO_4 were added and the bottle was covered and shaken for 15 min. The purpose of cooling and covering the solution was to reduce free radical substitution. After shaking, 25 ml of 0.100 M I_2 was added and the entire solution titrated with Na_2SO_3.

There are four reactions of importance; the first occurs when the H_2SO_4 is added to bottle;

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3H_2O + 3Br_2$$

The Br_2 adds quantitatively to the double bond of the acrylic acid:

$$Br_2 + CH_2{=}CHCOOH \rightarrow BrCH_2BrCHCOOH$$

This is the most important step. The solution is shaken to allow complete reaction and kept covered to eliminate the formation of bromine radicals. The addition of the KI consumes the excess Br_2:

$$3I^- + Br_2 \rightarrow I_3^- + 2Br^-$$

Titration with $Na_2S_2O_3$ determines the excess amount of I_2. The normality of the acrylic acid is calculated with the following equation:

$$N_{AA} = \frac{NV - nv}{V_s}$$

where N_{AA} = normality of acrylic acid

N = normality of BrO_3^-/Br^- solution

V = volume of BrO_3^-/Br^- solution

n = normality of $Na_2S_2O_3$

v = volume of $Na_2S_2O_3$

V_s = sample volume

The accuracy of this method is within 5% of the actual value.

APPENDIX 1-G

ICE

The concentration of acrylic acid in hydration experiments was followed by ion chromatography exclusion (ICE). A set of three standards of acrylic acid with concentrations ranging from 0.2 mM to 0.05 mM were run on the ion chromatograph. A calibration curve of concentration versus peak height was prepared. The response of ICE was linear.

Samples were taken and diluted by a factor of 10,000 which effectively quenched the reaction. The diluted sample was then run on the ion chromatograph and the concentration of the acrylic acid determined with the calibration curve. It was also possible to detect polyacrylic and hydroxypropionic acids. No standards existed for these acids, therefore it was impossible to determine the concentrations. The elution times for acrylic and hydroxypropionic acids using 0.1 mM HCl as the eluent and a flow rate of 0.91 ml/min were, respectively, 20 min and 18 min. The elution time of polyacrylic acid depended on the degree of polymerization but was always less than 17 min.

APPENDIX 1-H

IODINE TITRATION

Samples containing sulfite or bisulfite were anlyzed by the following method. A one or two ml sample from the reaction mixture containing 0.20 M $SO_3^=$ or less was quenched by adding 10% excess 0.055 M I_2. This solution was then titrated to the starch endpoint with 0.002 M $Na_2S_2O_3$ to determine the amount of excess I_2. The sulfite was then determined by difference.

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SECTION 2

ENHANCED ABSORPTION OF SULFUR DIOXIDE BY SULFITE AND OTHER BUFFERS

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SECTION 2

ABSTRACT

One practical method for stack gas desulfurization is scrubbing with a $CaO/CaCO_3$ slurry. Both alkalis and buffers have been proposed as mass transfer enhancing additives for slurry systems. Experiments were performed at 55°C by absorbing sulfur dioxide gas (2000-5000 ppm) with absorbing solutions across an unbroken gas-liquid interface with solutions containing sulfite, sulfate, and six different buffers in the presence of Na^+, Mg^{++}, or Ca^{++}. A model was developed to predict mass transfer behavior as a function of solution and gas composition using an approximation of surface renewal theory with multiple equilibrium reactions. Interactions of Ca^{++} and Mg^{++} with anions not only shifted buffer equilibria but also reduced diffusivities of univalent and bivalent anions by 25 and 45%, respectively. Therefore, sodium and magnesium alkali additives provide equal mass transfer enhancement. Twelve buffers were modeled for mass transfer enhancement. The most cost effective buffers were adipic, glycolic, sulfosuccinic, and hydroxypropionic acids.

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CHAPTER 2-1

INTRODUCTION

A flue gas desulfurization (FGD) process must reduce the sulfur oxides concentration to environmentally acceptable levels as well as dispose of the waste product by environmentally acceptable means. FGD systems attaining these goals can be divided into two categories: throwaway systems and regenerable systems. Both systems have commercially met government standards for sulfur oxide emissions. The research described in this thesis deals with gas/liquid mass transfer in $CaO/CaCO_3$ throwaway slurry scrubbing systems.

Of the methods considered, throwaway slurry scrubbing has been the most successful commercial process. It is conceptually simple and economically attractive. Sulfur dioxide is absorbed in an aqueous slurry of $CaSO_3/CaSO_4$ product solids with excess $CaCO_3$. Lime (CaO) or limestone ($CaCO_3$) is added as a raw material to neutralize sulfur dioxide and precipitate calcium sulfite/calcium sulfate. The product solids are separated and disposed of as a solid waste. The present research deals with simple slurry scrubbing and with modifications using alkali additives, buffer additives, or forced oxidation.

BACKGROUND

Simple Slurry Scrubbing

A schematic diagram of simple slurry scrubbing is shown in Figure 2-1. The major components of the process are the scrubber, the crystallizer, and the liquid-solid separator.

In the scrubber sulfur dioxide is absorbed into a slurry of $CaSO_3$, $CaSO_4$, and excess limestone (or lime depending on the raw material used). The slurry flows into a crystallizer, is neutralized with lime or limestone, and is recycled to the scrubber. A bleed stream is fed to a liquid-solid separator from which the liquid is recycled to the scrubber and the solids are removed as a waste product.

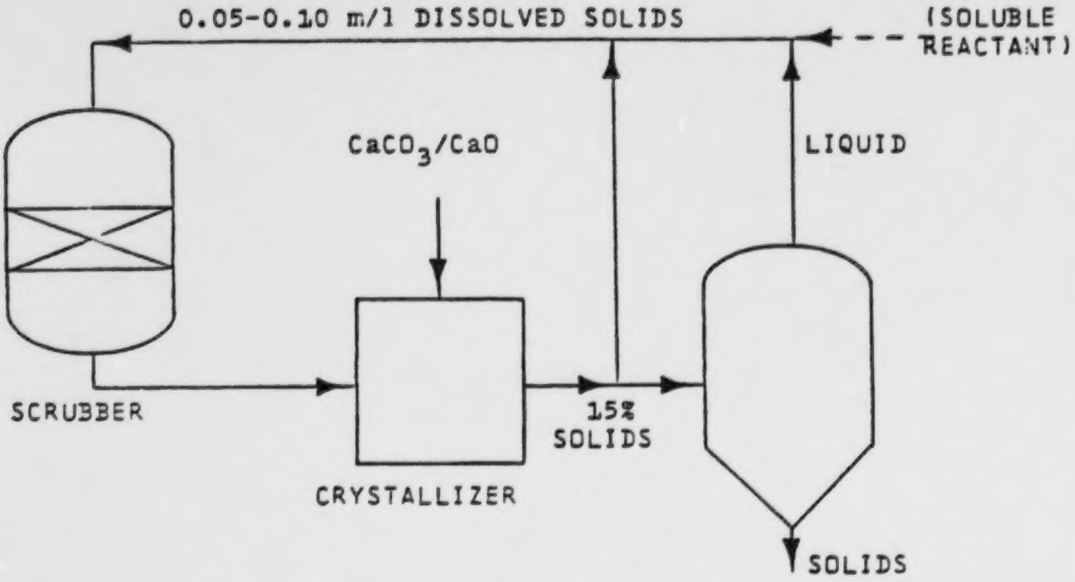

0.05-0.10 m/l DISSOLVED SOLIDS
(SOLUBLE REACTANT)
$CaCO_3/CaO$
LIQUID
SCRUBBER
15% SOLIDS
CRYSTALLIZER
SOLIDS

Figure 2-1. Simple Slurry Scrubbing

Sulfur dioxide absorption in pure water occurs by

$$SO_2(g) \longrightarrow SO_2(aq) \qquad 2\text{-}1$$

Once in the aqueous state a reversible hydrolysis reaction leads to the formation of bisulfite ions:

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+ \qquad 2\text{-}2$$

However, with a typical scrubber gas phase concentration of 2000 ppm SO_2, the equilibrium total sulfur dioxide concentration (SO_2 plus HSO_3^-) in the liquid phase is about 1 millimole/liter (mM) and the pH approximately 3. This low liquor SO_2 concentration results in an extremely large liquid flow rate through the scrubber and in a very small liquid phase driving force for mass transfer.

To reduce the high liquid flow rates required with pure water, dissolved alkalinity is supplied to neutralize the SO_2 being absorbed in the scrubbing system. This results in better sulfur dioxide removal through

$$SO_2 + 2\ OH^- \longrightarrow SO_3^= + H\ O \qquad 2\text{-}3$$

or the equilibrium reaction

$$SO_2 + SO_3^= + H_2O \rightleftharpoons 2\ HSO_3^- \qquad 2\text{-}4$$

One way to provide this alkalinity is with the dissolution of alkaline solids in the scrubber. Reactions 2-3 and 2-4 indicate that addition of hydroxide or sulfite ions is beneficial. These could be added in the form of lime (calcium oxide) or calcium sulfite, both would supply the needed alkalinity:

$$CaO(s) + SO_2 \longrightarrow Ca^{++} + SO_3^= \qquad 2\text{-}5$$

and

$$CaSO_3(s) + SO_2 + H_2O \longrightarrow Ca^{++} + 2\ HSO_3^- \qquad 2\text{-}6$$

An inexpensive way to provide the alkalinity is with limestone. An additional benefit derived from limestone utilization is the presence of bicarbonate, also a soluble alkaline species, which is released upon limestone dissolution:

$$CaCO_3(s) + HSO_3^- \longrightarrow CaSO_3 + HCO_3^- \qquad 2\text{-}7$$

where the bicarbonate can react directly with the sulfur dioxide:

$$HCO_3^- + SO_2 \longrightarrow CO_2 + HSO_3^- \qquad 2\text{-}8$$

and the calcium sulfite can also react with sulfur dioxide (2-6).

The system of reactions for sulfur dioxide absorption is controlled by two mass transfer phenomena: 1) the solid dissolution and transport in the bulk liquid, and 2) the gas absorption and subsequent transport in the bulk liquid. The solid dissolution rate is important for sizing a crystallizer and for its effect on the alkalinity of the scrubbing solution. But due to the presence of alkalinity already in the solution the more critical problem is the rate of SO_2 absorption from the gas or the liquid. An increased absorption rate would improve the sulfur dioxide removal efficiency and improve limestone utilization in existing systems. In new designs, an increased rate of absorption will result in a smaller diameter column which could utilize operating advantages such as lower pressure drop and lower liquid flow rates.

The gas-liquid sulfur dioxide transfer has been found to be a liquid phase controlled mechanism under slurry scrubbing conditions (Rochelle and King, 1979; Chang, 1979). Therefore, work done in enhancing the mass overall transfer rate should initially concentrate on the liquid phase. To increase the liquid-side rate, alkalinity must be provided at the interface in order for sulfur dioxide reactions to occur. Several investigators have recognized this and two approaches have been proposed: 1) the addition of soluble alkali additives, and 2) the addition of buffer additives.

Alkali Additives

One way to increase the alkalinity is to add soluble sulfites, sulfates, carbonates, or hydroxides to the system. Soluble alkalis can be added through magnesium, sodium, ammonia, and amine compounds which exhibit characteristics necessary to provide the extra alkalinity needed. While several compounds are physically practical, MgO and Na_2CO_3 combine physical practicality with reasonable cost, making them the most attractive.

In a simple slurry system the soluble alkalis accumulate primarily as soluble sulfites. The concentration of soluble sulfite is proportional to the concentration of sulfate (or alkali) because of the equilibrium

$$CaSO_4(s) + SO_3^{=} \rightleftharpoons CaSO_3(s) + SO_4^{=} \qquad 2\text{-}9$$

From this reaction an equilibrium relation can be developed

$$[SO_3] \ \alpha \ [SO_4] \times (a_{CaSO_3}/a_{CaSO_4}) \qquad 2\text{-}10$$

where a represents thermodynamic activity. The equilibrium relation shows a direct correlation between the sulfate and sulfite concentrations present. The sulfite ions can then be used to neutralize the sulfur dioxide, Reaction 1-4, forming bisulfite. Dissolved sulfate can also have a positive effect on SO_2 mass transfer, by the buffering effect of $SO_4^{=}/HSO_4^{-}$.

The equilibrium reaction presented in Eq. 2-10 shows the inverse relationship between the dissolved sulfite concentration and the gypsum ($CaSO_4$) activity. When the solids oxidation is less than 20%, the activity of gypsum is less than one because $CaSO_4$ forms a solid solution with $CaSO_3 \cdot \frac{1}{2}H_2O$ (Rochelle, 1977). Therefore, there is a greater concentration of dissolved sulfite giving better mass transfer.

The actual mechanism of absorption in alkali additive systems can be demonstrated with sodium carbonate. The Na_2CO_3 reacts with sulfur dioxide in the presence of gypsum:

$$Na_2CO_3 + SO_2 + CaSO_4 \rightleftharpoons 2\ Na^+ + CO_2 + CaSO_3(s) + SO_4^{=} \qquad 2\text{-}11$$

thus producing dissolved sulfate. In this case the amount of sodium carbonate added is directly proportional to the amount of sulfate produced. This excess sulfate then produces sulfite, through the equilibrium liquid-solid relation (Reaction 2-9), which is free to interact with the SO_2.

In the magnesium case, ion pairing becomes significant and the process of sulfate formation and sulfite equilibrium is more complex. The initial reaction with magnesium oxide resembles the carbonate reaction

$$MgO + SO_2 + CaSO_4(s) \rightleftharpoons CaSO_3(s) + Mg^{++} + SO_4 \qquad 2\text{-}12$$

Once again the sulfate from this relation can interact with the system solids to form the desired sulfite. However, in this system the free magnesium ion present in solution tends to ion pair with dissolved anions (sulfites, sulfates)

$$Mg^{++} + SO_3^{=} \rightleftharpoons MgSO_3^{\circ} \qquad 2\text{-}13$$

where the superscript zero represents an ion pair. This ion pair interaction results in a new equilibrium reaction

$$CaSO_4(s) + MgSO_3^{\circ} \rightleftharpoons CaSO_3^{\circ} + MgSO_4 \qquad 2\text{-}14$$

This ion pair-solids equilibrium combines with the sulfite-sulfate liquid-solid equilibrium, Reaction 2-9, to increase both the total sulfate and the total sulfite concentrations. This, in turn, increases the sulfur dioxide removal capacity of the system.

The additional alkalinity present in the magnesium system is accompanied by reduced diffusivity. The magnesium ion pair has a lower diffusivity than the sulfite ion. While more total sulfite ion is present in the magnesium system, the ion cannot diffuse to the sulfur dioxide as rapidly as free sulfite ions, limiting its effectiveness. In practice, the extra alkalinity present and the lower diffusivity balance each other out, giving the same results found with sodium carbonate.

Direct addition of sulfate groups should also increase the capabilities of the system. Sulfates can come from two internal sources at a coal fired power plant: cooling water blowdown or flyash. The sulfates from these sources would be in the form of $MgSO_4$ and Na_2SO_4. The sulfate would act in the presence of system solids to form gypsum and sulfite ion, releasing the sulfite to interact with the sulfur dioxide. The advantage of this proposal is the cheap source of raw materials.

One last point in alkali additives concerns the adverse effect of chloride ions on the scrubbing system. Chlorides are present in the flue gas as well as in the power plant sources of sulfates. The adverse effect is illustrated in an argument involving magnesium additives:

$$MgO + SO_2 + Ca^{++} + 2\ Cl^- \rightarrow Mg^{++} + 2\ Cl^- + CaSO_3(s) \qquad 2\text{-}15$$

This demonstrates that as long as there is excess chloride in the system, neutrality requires free cations to exist also. These free cations are calcium ions which react with the sulfur dioxide and the magnesium oxide to form $CaSO_3(s)$. However, no sulfite is produced; this means that in systems with chloride present more additive is required to achieve the same removal.

Buffer Additives

Another way to affect sulfur dioxide mass transfer is with soluble buffer additives. The buffer capacity and buffer diffusivity have a direct impact on the mass transfer (Rochelle, 1977; Chang, 1979). Other characteristics that must be investigated when choosing additives include volatility, solubility, toxicity, and cost.

Buffer capacity is the amount of buffer that functions as an alkali under scrubber conditions. If the buffer pK_a (effective equilibrium constant) is in the scrubber operating pH range, the buffer capacity approaches the concentration of the additive. However, if the pK_a is not in the pH range of the scrubber, the buffer capacity can be estimated (Rochelle, 1977) by

$$\text{Buffer Capacity} = [\text{additive}]\ 10^{-[\text{pH}-\text{p}K_a]} \qquad (2\text{-}16)$$

where the pH value used is the scrubber pH value nearest to the pK_a. Typically scrubbers operate in the pH range of 4.0 - 5.5, with forced oxidation systems on the low pH side and non-forced oxidation systems on the high side. So an additive with a pK_a in the range of 4-5 would work well in both systems.

Diffusivity of the buffer and its ionic species is also very important to the mass transfer rate of sulfur dioxide (Chang, 1979). The diffusivity governs movement of the buffer to the gas-liquid interface where it reacts with the sulfur dioxide as an alkali:

$$SO_2 + A^- + H_2O \longrightarrow HSO_3^- + HA \qquad 2\text{-}17$$

where HA represents the fully protonated buffer and A^- the dissociated buffer anion.

Taking these restrictions into consideration some carboxylic, sulfocarboxylic, and inorganic buffers have appeared to be good mass transfer enhancers. Investigations conducted both at the experimental and the pilot plant scale show several different additives can economically increase mass transfer capabilities.

Change (1979) identified several buffer additives that exhibit desirable mass transfer qualities. Six of the buffers identified by Chang were chosen for further investigation in this work. These six were: hydroxypropionic, sulfopropionic, sulfosuccinic, adipic, and acetic acids, as well as aluminum chloride. More specifically, the acetic acid was chosen to represent monofunctional buffers. Chemical Construction Co. has patented the use of acetic acid (Villiers-Fisher, 1972) as a result of experiments showing an increase in mass transfer capabilities with acid addition. Adipic acid is bifunctional and has been successful in increasing sulfur dioxide removal in pilot plant tests by EPA (Head, 1979). The sulfocarboxylic acids are considered because the sulfonic acid group is highly acidic and therefore fully dissociated at scrubber pH values, which means that the acids are essentially nonvolatile. Also, their buffer capacities are in the ideal range. Hydroxypropionic acid exhibits the same favorable characteristics as the sulfocarboxylic acids. In addition, it acts as an oxidation inhibitor. Aluminum sulfate is the only inorganic acid considered. It was chosen because it has good buffer capacity at low pH and because it is used in a clear solution scrubbing system (Ymamichi and Nagao, 1976).

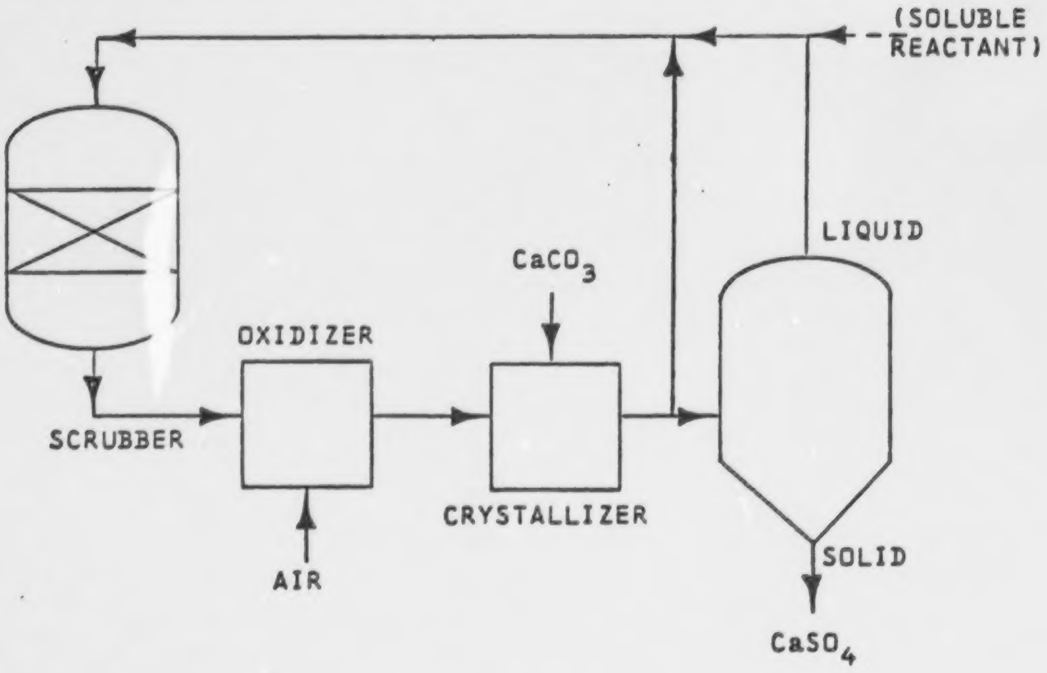
Forced Oxidation

The cost of additive makeup due to losses in the solid waste is significant in the economics of additive systems. A process step called "forced oxidation" can be incorporated into the slurry scrubbing system to reduce the additive loss. Such a step is shown in Figure 2-2 as air sparging of a slurry hold tank. Forced oxidation is used to oxidize $CaSO_3$ to gypsum ($CaSO_4 \cdot 2H_2O$). The resulting gypsum has better dewatering properties than normal waste ($CaSO_3/CaSO_4$). Therefore, more additive can be recovered from the waste product (Rochelle and King, 1977; Head et al., 1979). This applies to both alkali and buffer additive systems.

In alkali additive systems, dissolved sulfite interactions are the primary method of sulfur dioxide removal. Therefore, forced oxidation of the solid and dissolved sulfite would severely reduce the effectiveness of alkali additives. As a result, forced oxidation is not practical with the alkali additive system, unless performed on a bleed stream.

In the buffer additive case, the high cost of the additive makes recovery a significant factor in the economics of the system. Additionally, forced oxidation reduces the total sulfite concentration which in this case is beneficial. The total sulfite concentration at pH 4-5 (typical forced oxidation scrubbing conditions) is predominantly present as bisulfite (Head et al., 1977). Bisulfite detracts from the performance of the scrubber due to

Figure 2-2. Slurry Scrubbing with Forced Oxidation


(SOLUBLE REACTANT)
LIQUID
$CaCO_3$
OXIDIZER
SCRUBBER
CRYSTALLIZER
AIR
SOLID
$CaSO_4$

the depression of

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+ \qquad 2\text{-}2$$

Thus, the reduction of the total sulfite concentration enhances sulfur dioxide mass transfer in a system which does not rely upon sulfite to produce its alkalinity.

Forced oxidation can also have a harmful effect on the degradation of organic buffers (Rochelle, 1977; Garcia, 1980). This degradation translates to a loss of active buffer capacity and the possibility of harmful environmental effects. So far degradation has not been quantified, but when it is, degradation must be weighed against the savings realized in additive recovery.

OBJECTIVES

It is apparent that slurry scrubbing is a complicated system of simultaneous equilibria dependent on mass transfer. This section has also illustrated that system additives provide the possibility of sulfur dioxide absorption improvement due to their effects on the rate of gas-liquid mass transfer. The objective of this work is to adjust the gas-liquid mass transfer model developed by Chang and Rochelle (Chang, 1979) to make it applicable to slurry scrubbing.

Chang (1979) developed and tested a mass transfer model which considered sulfur dioxide absorption as a function of both gas and solution composition. This enhancement model was based on surface renewal theory and included a set of equilibrium reactions which were capable of handling buffer additives as well as simple systems. The model was verified by experiments at 25°C in 0.3 M NaCl with less than 1.0 mM of total dissolved sulfite.

In this work, the model has been modified for and confirmed by experiments at slurry conditions. The temperature was increased to 55°C, a typical SO_2 scrubbing temperature. A modified experimental technique permitted operation with high dissolved sulfite. Experiments in Ca^{++} and Mg^{++} electrolytes showed that diffusivities must be reduced because of the effects of ion pairing.

The experiments conducted by Chang were reproduced at 55°C with both univalent and bivalent cations (Na^+, Mg^{++}, Ca^{++}) to quantify ion pairing effects as they would actually occur in the scrubbing solution. Other experiments performed considered high dissolved sulfur dioxide concentrations as well as sulfate and the effects of six buffers: acetic, adipic, hydroxypropionic, sulfopropionic, and sulfosuccinic acids and aluminum chloride.

Quantification of these systems with respect to the model gave a good basis for an economic analysis of additive alternatives in terms of absorption rates. It also allowed a more complete analysis of these flue gas desulfurization processes.

CHAPTER 2-2

THEORY

This thesis deals with the rate of sulfur dioxide absorption in aqueous solutions. According to interfacial mass transfer theory, the rate of absorption can be represented as

$$N_{SO_2} = k_g(p_{SO_2} - p_{SO_{2i}}) = k_l(C_{SO_{2i}} - C_{SO_2})$$

where k_g and k_l are the gas and liquid phase mass transfer coefficients, N_{SO2} represents the rate of mass transfer across the interface per unit area, and the subscript i designates interface conditions. The rate of absorption is enhanced by equilibrium reactions in the liquid phase boundary layer. This enhancement is represented by Sherwood, Pigford, and Wilke (1975) as

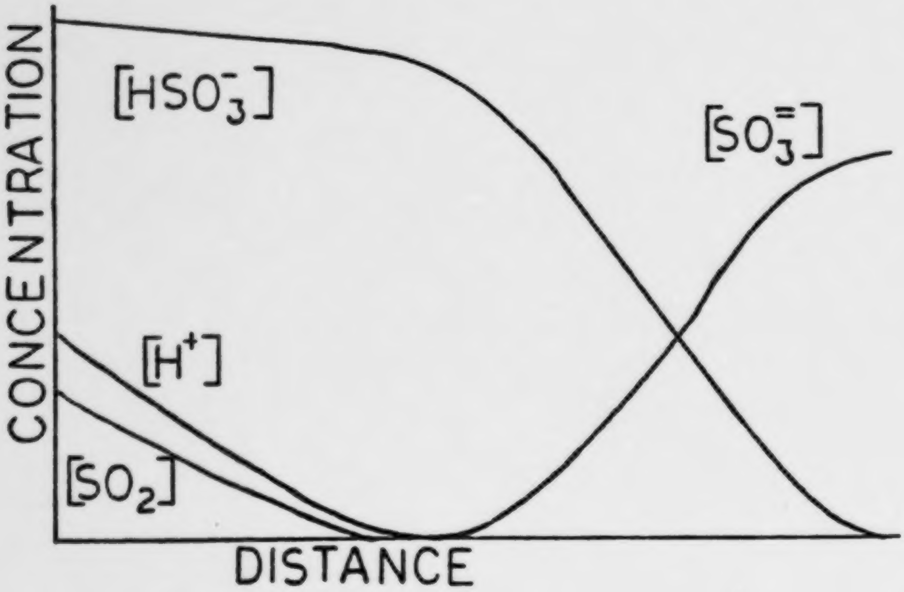
$$\phi = k_l/k_l^\circ$$

where k_l° represents the physical absorption mass transfer coefficient, the mass transfer coefficient without any chemical reactions.

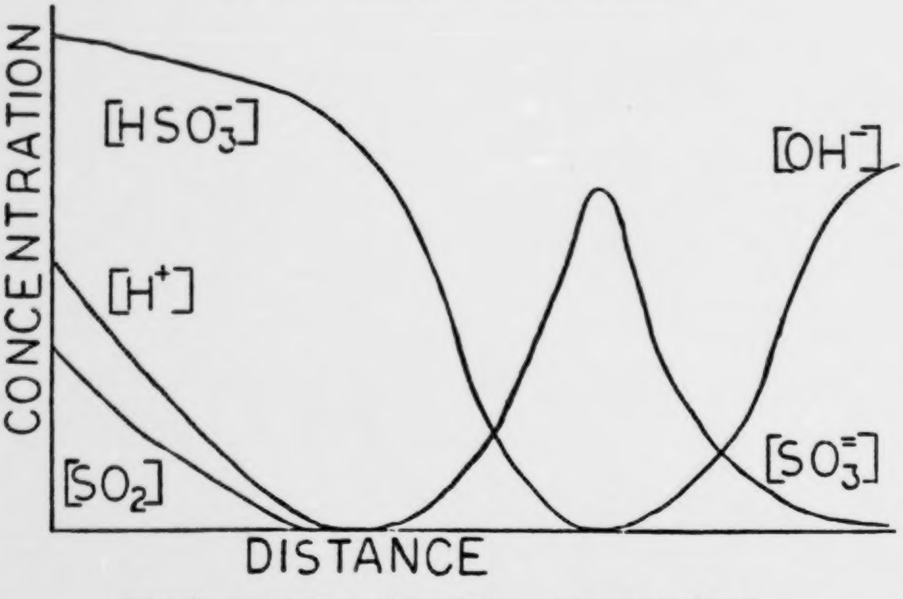
Figure 2-3 shows a concentration gradient diagram near the gas-liquid interface. The diagram qualitatively illustrates the effects of the reactions as a function of distance from the interface. The pH value at the interface is lower than the pH value in the bulk solution. This restricts the hydrolysis reaction from occurring at the interface and contributes to the sulfur dioxide concentration decrease between the interface and the bulk.

The effects of additives are easily described with Figure 2-3. Alkali additives increase the sulfite concentration, thus contributing to more sulfur dioxide absorption through the sulfite equilibrium, Eq. 2-2. Buffer additives contribute by reducing the hydrogen ion concentration at the interface, thus affecting the hydrolysis reaction, Eq. 2-1.

Chang (1979) developed an enhancement factor model to determine the liquid phase resistance of sulfur dioxide absorption in complex environments. This enhancement model can be divided into two parts. The first involves the



Species Interaction Near the Interface
without Excess Alkali Added



Species Interaction Near the Interface
with Excess Alkali Added

Figure 2-3. Qualitative View of the Gas-Liquid Interface

absorption mechanism, reactions that occur during absorption, and the second includes the implementation of the surface renewal theory of mass transfer.

CHEMICAL ABSORPTION MECHANISM

When sulfur dioxide is absorbed into aqueous solutions of difunctional buffers, like adipic acid, at pH 2-9, the following four reversible reactions should be considered:

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^- \qquad 2\text{-}18$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^= \qquad 2\text{-}19$$

$$H_2A \rightleftharpoons H^+ + HA^- \qquad 2\text{-}20$$

$$HA^- \rightleftharpoons H^+ + A^= \qquad 2\text{-}21$$

where H_2A represents the fully protonated buffer and HA^- and $A^=$ represents its partially and fully dissociated ions, respectively.

Reaction 2-18 corresponds to the hydrolysis of absorbed SO_2. Its forward reaction rate constant is 3.4×10^6 sec^{-1} at 20°C (Eigen et al., 1961). Reactions 2-19, 2-20, and 2-21 are proton transfer reactions and, thus, have much higher reaction rates than Reaction 2-18. Due to the extremely fast rates, all four reactions are regarded as instantaneous for mass transfer modeling purposes. This is justified by Huang and Kuo (1965) who found that with fast reactions, such as these, the reaction rate constants become insignificant variables in the mass transfer rate expression.

The equilibrium constants, K_1, K_2, K_3, K_4 of Reactions 2-18, 2-19, 2-20, and 2-21, respectively, are represented by

$$K_1 = (a_{H^+})(a_{HSO_3^-})/(a_{SO_2}) = 1.3\times10^{-2}$$

(Johnstone and Leppla, 1934)

$$K_2 = (a_{H_3^+})(a_{SO^=})/(a_{HSO_3^-}) = 6.2\times10^{-8}$$

(Tartar and Garretson, 1941)

$$K_3 = (a_{H^+})(a_{HA^-})/(a_{H_2A})$$

$$K_4 = (a_{H^+})(a_{A^=})/(a_{HA^-}) \quad .$$

at 25°C and infinite dilution. Values of K_3 and K_4 pertain to the specific buffer used. For example, with adipic acid $K_3=3.81\times10^{-5}$ and $K_4=3.87\times10^{-6}$ (Gane and Ingold, 1931). The equilibrium constants expressed here indicate that Reactions 2-18 to 2-21 will participate in the mass transfer of SO_2 at typical scrubber pH values of 3-6. Therefore, SO_2 absorption in a $CaO/CaCO_3$ slurry scrubber is a process of mass transfer with multiple, instantaneous, reversible reactions.

Chang (1979) developed a model to approximate surface renewal theory with this set of equilibrium reactions. Surface renewal theory describes mass transfer as diffusion into an interfacial element which is displaced after time, t, by a fresh element in which diffusion can take place.

According to surface renewal theory, the material and charge balances for Reactions 2-18 to 2-21 are:

$$D_{SO_2}\frac{\partial^2[SO_2]}{\partial x^2} + D_{HSO_3^-}\frac{\partial^2[HSO_3]}{\partial x^2} + D_{SO_3^-}\frac{\partial^2[SO_3^{=}]}{\partial x^2} = \frac{\partial[SO_2]}{\partial t} + \frac{\partial[HSO_3^-]}{\partial t} + \frac{\partial[SO_3^{=}]}{\partial t} \qquad 2\text{-}22$$

$$D_{H_2A}\frac{\partial^2[H_2A]}{\partial x^2} + D_{HA^-}\frac{\partial^2[HA^-]}{\partial x^2} + D_{A^{=}}\frac{\partial^2[A^{=}]}{\partial x^2} = \frac{\partial[H_2A]}{\partial t} + \frac{\partial[HA^-]}{\partial t} + \frac{\partial[A^{=}]}{\partial t} \qquad 2\text{-}23$$

$$D_{H^+}\frac{\partial^2[H^+]}{\partial x^2} - D_{HSO_3^-}\frac{\partial^2[HSO_3^-]}{\partial x^2} - 2D_{SO_3^{=}}\frac{\partial^2[SO_3^{=}]}{\partial x^2} - D_{HA^-}\frac{\partial^2[HA^-]}{\partial x^2} - 2D_{A^{=}}\frac{\partial^2[A^{=}]}{\partial x^2} = \frac{\partial[H^+]}{\partial t} - \frac{\partial[HSO_3^-]}{\partial t} - 2\frac{\partial[SO_3^{=}]}{\partial t} - \frac{\partial[HA^-]}{\partial t} - \frac{\partial[A^{=}]}{\partial t} \qquad 2\text{-}24$$

Assuming that the chemical equilibrium relations of Reactions 2-18 to 2-21 are effective at any point in the liquid phase, three non-linear second order partial differential equations with three unknowns can be obtained by substituting the equilibrium relations into equations 2-22, 2-23, and 2-24. There is no analytical solution for this set of equations, but an approximate analytical solution can be obtained by replacing the diffusivity ratios in the solution of the film theory steady state model by their square roots (Chang, 1979). The general solutions to the film theory material balance equations are:

$$D_{SO_2}[SO_2] + D_{HSO_3^-}[HSO_3^-] + D_{SO_3^=}[SO_3^=] = b_1x + b_2 \qquad \text{2-25}$$

$$D_{H_2A}[H_2A] + D_{HA^-}[HA^-] + D_{A^=}[A^=] = b_3x + b_4 \qquad \text{2-26}$$

$$D_{H^+}[H^+] - D_{HSO_3^-}[HSO_3^-] - 2D_{SO_3^=}[SO_3^=] - D_{HA^-}[HA^-]$$

$$- 2D_{A^=}[A^=] = b_5x + b_6 \qquad \text{2-27}$$

All of these concentrations are subject to the equilibrium relations of Reactions 2-18 to 2-21. The boundary conditions are:

at $x=0$, $[SO_2]=[SO_2]_i$, $D_{SO_2}\dfrac{d[SO_2]}{dx} + D_{HSO_3^-}\dfrac{d[HSO_3^-]}{dx} + D_{SO_3^=}\dfrac{d[SO_3^=]}{dx} = b_1$ 2-28

$$D_{H_2A}\frac{d[H_2A]}{dx} + D_{HA^-}\frac{d[HA^-]}{dx} = D_{A^=}\frac{d[A^=]}{dx} = 0 = b_3 \qquad \text{2-29}$$

$$D_{H^+}\frac{d[H^+]}{dx} - D_{HSO_3^-}\frac{d[HSO_3]}{dx} - 2D_{SO_3^=}\frac{d[SO_3^=]}{dx} - D_{HA^-}\frac{d[HA^-]}{dx}$$

$$- 2D_{A^=}\frac{d[A^=]}{dx} = 0 = b_5 \qquad \text{2-30}$$

at $x=\delta$, $[SO_2]=[SO_2]_o$, $[H^+]=[H^+]_o$, $[H_2A]=[H_2A]_o$
where $[SO_2]_i$ represents the physical solubility of sulfur dioxide. Differential Eq. 2-28 is a representation of the flux of SO_2 through the gas-liquid interface, while differential Eqs. 2-29 and 2-30 reflect the inability of the other species to penetrate the surface.

The approximate surface renewal theory mass transfer enhancement factor can be written as:

$$\phi = 1 + \Big[D_{H^+}^{1/2}([H^+]_i - [H^+]) - D_{SO_3^=}^{1/2}([SO_3^=]_i - [SO_3^=])$$

$$- 2D_{A^=}^{1/2}([A^=]_i - [A^=]) - D_{HA^-}^{1/2}([HA^-]_i - [HA^-])\Big] /$$

$$D_{SO_2}^{1/2}([SO_2]_i - [SO_2]) \qquad \text{2-31}$$

The values of all of the concentrations at the gas-liquid interface can be estimated by solving the fifth order algebraic equation derived from Eqs. 2-26, 2-27, and 2-28 and their boundary conditions, replacing all of their diffusivity ratios by their square roots. This was solved by the computer program in Appendix 2-B.

This mass transfer model can also be employed with monofunctional buffers or without any buffer added. For monofunctional buffers, like acetic acid, the enhancement factor can be obtained using the single buffer equilibrium constant for K_3 and a dummy value, such as 10^{-15}, for K_4. For finding the enhancement in the absence of a buffer, a buffer concentration of zero is inserted into the model, thus eliminating the effect of additives in the system.

Buffers with pK_a values outside the normal operating range, such as sulfite, are treated in the same way as normal buffers. This includes hydroxide which can be modeled by treating water as a monofunctional buffer.

MODELING SLURRY SCRUBBING

Typical slurry scrubbing operating conditions are listed in Table 2-1. These conditions illustrate the need to operate the model at 55°C and with dissolved calcium ions present. Operating at 55°C requires minor adjustments in equilibrium constants and diffusivities while the presence of calcium ions results in the more complex problem of ion pairing.

Ion pairing and its effects on equilibrium constants are demonstrated here with Ca^{++} and $SO_3^=$:

$$Ca^{++} + SO_3^= \rightleftharpoons CaSO_3^\circ \qquad 2\text{-}32$$

$$K_{CaSO_3^\circ} = (a_{CaSO_3^\circ})/(a_{Ca^{++}})(a_{SO_3^=}) \qquad 2\text{-}33$$

Assuming that $CaSO_3^\circ$ can react with dissolved SO_2 like a sulfite ion, there is no lost alkalinity by the presence of the ion pair. Therefore, a modified equilibrium constant for Reaction 2-19 can be used to account for the calcium effects on the equilibrium:

Table 2-1: Typical Conditions in a CaO/$CaCO_3$ Slurry Scrubber

Temperature, °C	55
Concentration of Sulfur Dioxide, ppm	
Entering	500 to 5000
Leaving	20 to 200
Hydrogen Ion Concentration, pH	4.5 to 5.5
Total Dissolved Sulfite, mM	0 to 20
Total Dissolved Calcium, mM	0.05 to 0.2

Table 2-2: Physical Properties at 55°C, 0.3 M NaCl

Buffer	Diffusivitiesx10^5 (cm^2/sec)			pK_a[d] Values	
	H_2A	HA	A	pK_1	pK_2
Acetic		1.19[a]	1.09[a]	4.06	
Adipic	0.74[a]	0.72[a]	0.65[a]	4.07	5.10
Benzoic		1.21[a]	0.87[a]	4.05[b]	
Formic		1.46[a]	1.43[a]	3.60[b]	
Glycolic		0.98[a]	0.91[a]	3.60[b]	
Hydroxypropionic		0.90[a]	0.80[a]	4.33[b]	
Lactic		0.99[a]	0.80[a]	3.60[b]	
Phthalic	0.72[a]	0.71[a]	0.69[a]	3.02	4.6
Succinic	0.86[a]	0.84	0.81[a]	4.10	4.90
Sulfopropionic		0.45	0.40	4.06	
Sulfosuccinic	0.73[a]	0.70[a]	0.66[a]	3.33[b]	4.84
Sulfate		1.20[a]	0.90[a]	1.55[c]	
Sulfite	2.00[a]	1.33[a]	0.98[a]	2.02[a]	7.4

---

[a] from Chang (1979)
[b] from Cavanaugh (1978)
[c] from Radian Equilibrium Program
[d] $K_a = a_{H^+}[A^-]/[HA]$

$$K = (a_{H^+})(a'_{SO_3^=})/(a_{HSO_3^-}) \qquad 2\text{-}34$$

where $$a'_{SO_3} = a_{SO_3^=}(1 + a_{Ca^{++}} K_{CaSO_3^\circ}) \qquad 2\text{-}35$$

Radian Corporation (Lowell et al., 1970) developed a computer program to find the equilibrium values of compounds that are commonly found in scrubbing systems. The Radian equilibrium program gives $K = 2.02 \times 10^{-6}$ M.

The effects of ion pairing and activity coefficients on buffer species were determined by experimental measurements of apparent equilibrium constants in 0.1 M $CaCl_2$ and 0.3 M NaCl by Cavanaugh (1978).

Ion pairing also affects the diffusivity values. Bivalent cations lower the expected diffusivity of the uni- and bivalent anions due to the formation of larger molecules which move slower. The slower movement between the bulk solution and the gas-liquid interface is reflected in an enhancement factor that is lower than with univalent cations at the same ionic strength and pK_a values.

Where ion pairing is present diffusivities of anionic species have been adjusted so that the experimental data fit the experimental model. This work results in a consistent decrease in diffusivity of 25% for univalent anions and 45% for bivalent anions in the presence of bivalent cations (see Tables 2-2 and 2-3).

PHYSICAL PROPERTIES

The concentration of undissociated sulfur dioxide in pure water is found from Henry's law:

$$C_{A_{iw}} = P_{SO_2}/H \qquad 2\text{-}36$$

where P_{SO_2} is the interfacial partial pressure of the sulfur dioxide in the gas phase. In this case, the Henry's constant correlation is (Rabe and Harris, 1963)

$$H = \exp(-9.3795 + 2851.1/T) \qquad 2\text{-}37$$

The equilibrium constant of the hydrolysis reaction, Eq. 2-18, is calculated from (Rabe and Harris, 1963)

Table 2-3: Physical Properties at 55°C, 0.1 M $CaCl_2$

Buffer	Diffusivitiesx10^5 (cm^2/sec)			pK_a^d Values	
	H_2A	HA	A	pK_1	pK_2
Acetic		1.19[a]	0.82	4.45	
Adipic	0.74[a]	0.54	0.36	3.98	4.86
Benzoic		1.21[a]	0.65	3.90[b]	
Formic		1.46[a]	1.07	3.45[b]	
Glycolic		0.98[a]	0.68	3.42[b]	
Hydroxypropionic		0.90[a]	0.60	4.26[b]	
Lactic		0.99[a]	0.68	3.36	
Phthalic	0.72[a]	0.53	0.38	2.82[b]	4.4
Succinic	0.86[a]	0.53	0.45	3.98	4.60
Sulfopropionic		0.45	0.30	4.06[b]	
Sulfosuccinic	0.73[a]	0.53	0.36	3.14[b]	4.43
Sulfate		1.20[a]	0.68	1.60[c]	
Sulfite	2.00[a]	1.00	0.57	2.02[a]	6.2

---

[a] from Chang (1979)
[b] from Cavanaugh (1978)
[c] from Radian Equilibrium Program
[d] $K_a = a_H + [A^-]/[HA]$

$$K_a = \exp(-10.9670 + 1972.5/T) \qquad 2\text{-}38$$

with K_a in thermodynamic units.

Activity coefficients of ionic species were found from the Debye-Huckel limiting law (Lowell et al., 1970):

$$\log \gamma_j = 0.512\, n_j^2 \; (-I^{\frac{1}{2}}/1 + 0.312 c_{3j} I^{\frac{1}{2}}) + c_{4j} I \qquad 2\text{-}39$$

where n_j was the charge on the j^{th} ion; c_{3j} and c_{4j} were used to transform the equilibrium constant to concentration units, Table 2-4. The activity coefficient of hydrated sulfur dioxide in solution was estimated by (Harned and Owen, 1958):

$$\log \gamma = 0.076 \times I \qquad 2\text{-}40$$

The Radian equilibrium program (Lowell et al., 1970) provided the equilibrium constants for sulfate interactions, as a function of ionic strength at 55°C. This resulted in a pK_a of 1.60 for the $SO_4^=/HSO_4^-$ reaction.

Values for the effective equilibrium constants of the buffers, defined as $K_a = a_{H^+}[A^-]/[HA]$, are presented in Tables 2-2 and 2-3. These were primarily taken from acid-base titration experiments (Cavanaugh, 1978). Effective pK_a values in NaCl solutions were estimated from ideal and calcium based equilibrium constants. These values include effects of ion pairing and the activity coefficients of the buffer species.

The liquid phase diffusivity of sulfur dioxide in water was taken as 2.00×10^{-5} cm^2/sec at 30°C (Peaceman, 1951). The value at 25°C was then predicted using the Stokes-Einstein relation to correct for temperature and viscosity.

The true diffusivities of H^+, HSO_3^-, and $SO_3^=$ were calculated from ionic conductivities by

$$D_\pm = RT\, \lambda_\pm / n_j (Fa)^2 \qquad 2\text{-}41$$

where Fa is the Faraday number and $\lambda_\pm$ is the equivalent ionic conductivity. The ionic conductivities for H^+, HSO_3^-, and $SO_3^=$ at 25°C and infinite dilution were taken to be 350, 50, and 72 $cm^2/mmho$, respectively (Landolt and Bornstein, 1960).

Table 2-4: c_{3j}, c_{4j}: constants for estimation of the activity coefficients (Lowell, 1970)

	c_{3j}	c_{4j}
H^+	6.0	0.4
OH^-	3.0	0.3
HSO_3^-	4.5	0.0
$SO_3^=$	4.5	0.0

In pure water the condition of electrical neutrality requires an electric potential gradient to develop, slowing down the H^+ and increasing the movement of the other ions (Newman, 1967). However, in solutions with a large excess of other ions (NaCl, $CaCl_2$), a concentration gradient of nondiffusing ions develops which tends to disperse the potential gradient. So, the diffusional interference of the electric potential gradient can be avoided if excess salt is distributed uniformly through the system (Vinograd and McBane, 1941). This is demonstrated in the Vinograd and McBane equation which showed the effective diffusivity of H^+ differed from its true value by less than 2% when the total ionic strength was 50 times higher than the bisulfite concentration (Chang, 1979). Therefore, the effective diffusivities of H^+, HSO_3^-, and $SO_3^=$ are assumed to be equal to their true diffusivities 9.37×10^{-5}, 1.33×10^{-5}, and 0.98×10^{-5} cm^2/sec, respectively, at 25°C.

The diffusivities of the buffer ions were initially assumed to be equal to their true diffusivities. The diffusivities of the buffer ions were obtained from the literature at 25°C where possible; otherwise they were estimated by the following equation for carboxylic acids (Albery, 1967)

$$\log D = -(4.04 + 0.491 \log V) \qquad 2\text{-}42$$

where V is the molecular volume of the organic acid estimated by the method of Le Bas (1915). It was assumed that carboxylic ions have the same diffusivity as their molecules. Some of these diffusivities were then used as first approximations in the model for development of the effective diffusivities, the diffusivities used to match the model with the experiments, shown in Table 2-2.

In using the model it was assumed that the diffusivity ratios were independent of temperature and viscosity, so the values at 25°C and infinite dilution were used. The model also reduces the diffusivity of the anions in a bivalent cation environment. As previously mentioned the univalent anions were reduced by 25% and the bivalent anions by 45%.

CHAPTER 2-3

EXPERIMENTAL APPARATUS AND PROCEDURE

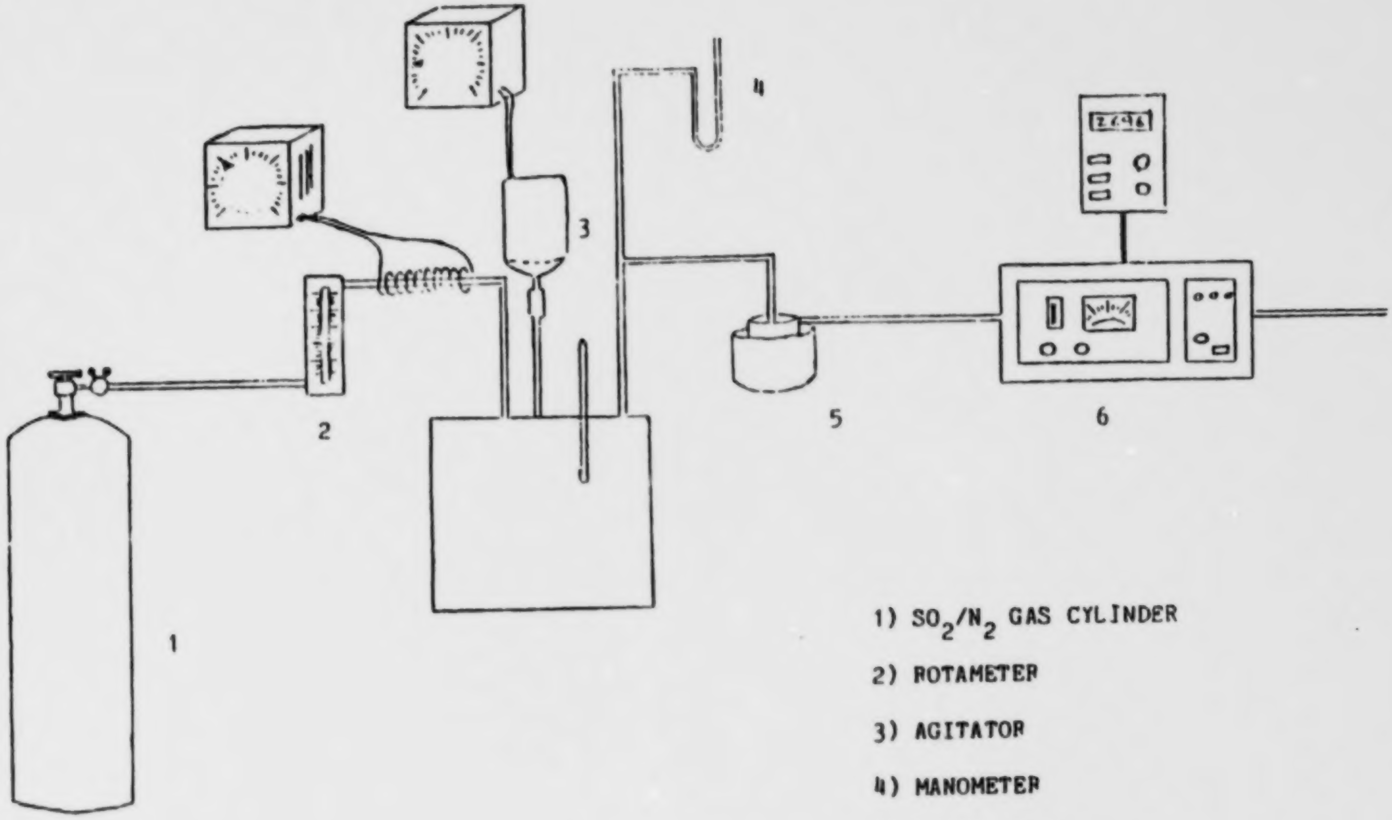
The experimental apparatus used in this analysis of sulfur dioxide absorption rates employed gas-liquid contacting in a stirred, 2 liter, 14 cm. ID reactor with continuous flow of both phases. The gas and liquid were contacted across an unbroken gas-liquid interface with mixing in both phases. Several independent material balances were performed with the characterization of the system to determine the experimental accuracy. Also several organic buffers identified as mass transfer enhancers were synthesized in the laboratory for experimental use.

EXPERIMENTAL APPARATUS

The sulfur dioxide-solution contacting apparatus is schematically shown in Figures 2-4 and 2-5. The continuous flow gas-liquid contactor consisted of an insulated, 14 cm ID, two liter, Lucite vessel with agitation provided in both phases. The pre-mixed SO_2/N_2 gas flow rate was measured with a rotameter. The gas outlet sulfur dioxide concentration was found using a Thermo-Electron Model 40 pulsed fluorescent SO_2 analyzer. A pre-mixed aqueous solution was delivered at a constant rate through a valve. Both the inlet and outlet streams were analyzed for sulfite by iodimetric titration.

Temperature control in the reactor was achieved by heating the reactor inlet streams with electrical resistance heating tape. The reactor temperature was measured with thermometers in both phases and was controlled by variacs connected to the heating tape. Heat loss through the reactor walls was minimized by one inch fiberglass insulation.

The reactor pH was controlled with continuous addition of 1.0 M sodium hydroxide directly into the reactor, to counteract the acidity formed in the hydrolysis reaction. This was accomplished with an infusion pump. The pH of the reactor outlet solution was continuously monitored with a Corning digital pH meter. This setup gave a 10 second lag time between variation in the NaOH



1) SO_2/N_2 GAS CYLINDER

2) ROTAMETER

3) AGITATOR

4) MANOMETER

5) LIQUID TRAP

6) SO_2 ANALYZER

Figure 2-4. Experimental Apparatus, Gas Phase

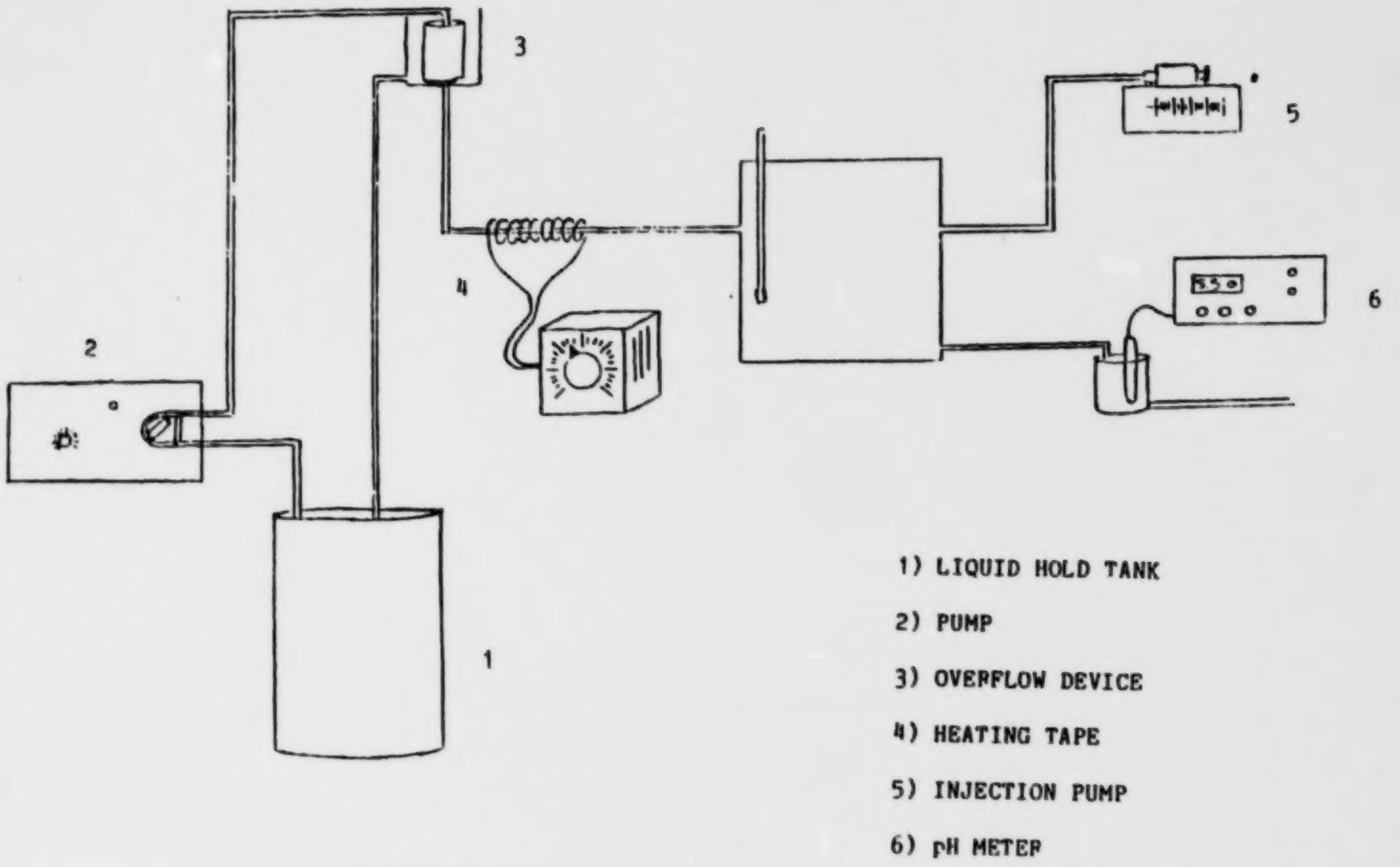

1
2
3
4
5
6
1) LIQUID HOLD TANK
2) PUMP
3) OVERFLOW DEVICE
4) HEATING TAPE
5) INJECTION PUMP
6) pH METER

Figure 2-5. Experimental Apparatus, Liquid Phase

injection rate and the pH response.

REACTOR

The insulated reactor, shown in Figure 6 was made of Lucite wrapped with one inch glass fiber insulation. Vortex formation was minimized by placing four equally spaced vertical baffles, each one-twelfth of the vessel width, on the vessel wall. Another baffle was attached on the gas inlet of the reactor to provide better gas distribution.

A 1/40 hp variable speed motor was used to drive the dual impeller polypropylene agitator. The agitator had a range of 0-6000 rpm, and mixed both the liquid and gas phases simultaneously. The gas phase stirrer, a paddle with three flat blades (Figures 2-6), was placed about one inch above the bottom of the vessel and horizontally centered.

In the range of 0-700 rpm an unbroken gas-liquid interface existed. At approximately 750 rpm gas was drawn into the liquid phase forming a vortex and thus increasing the total interfacial area between the liquid and gas phases. Above speeds of 1600 rpm liquid particles were entrained in the gas phase, so the maximum useful agitator speed was near 1500 rpm.

GAS MIXING

The SO_2/N_2 gas mixtures used in the experiments were prepared in the laboratory by mixing pure SO_2 with N_2 gas to give a gas containing approximately 20,000 ppm SO_2. A high pressure gas cylinder was vented to atmospheric pressure and purged with nitrogen before use. Pure SO_2 was added to the cylinder, approximately 20 psig, with nitrogen added to a final pressure of around 1000 psig. The cylinder was then allowed to equilibrate for two weeks before testing the final concentration.

The final sulfur dioxide level was checked by iodimetric titration with the dynamic saturation apparatus shown in Figure 2-7. The gas flowed into an absorbing starch solution contained in the gas washing bottle; the gas washing bottle also contained a pre-measured amount of iodine. The gas was passed through the washing bottle until the starch endpoint was reached. The volume of unreacted gas used in the titration was measured with a wet test flowmeter attached to the washing bottle.

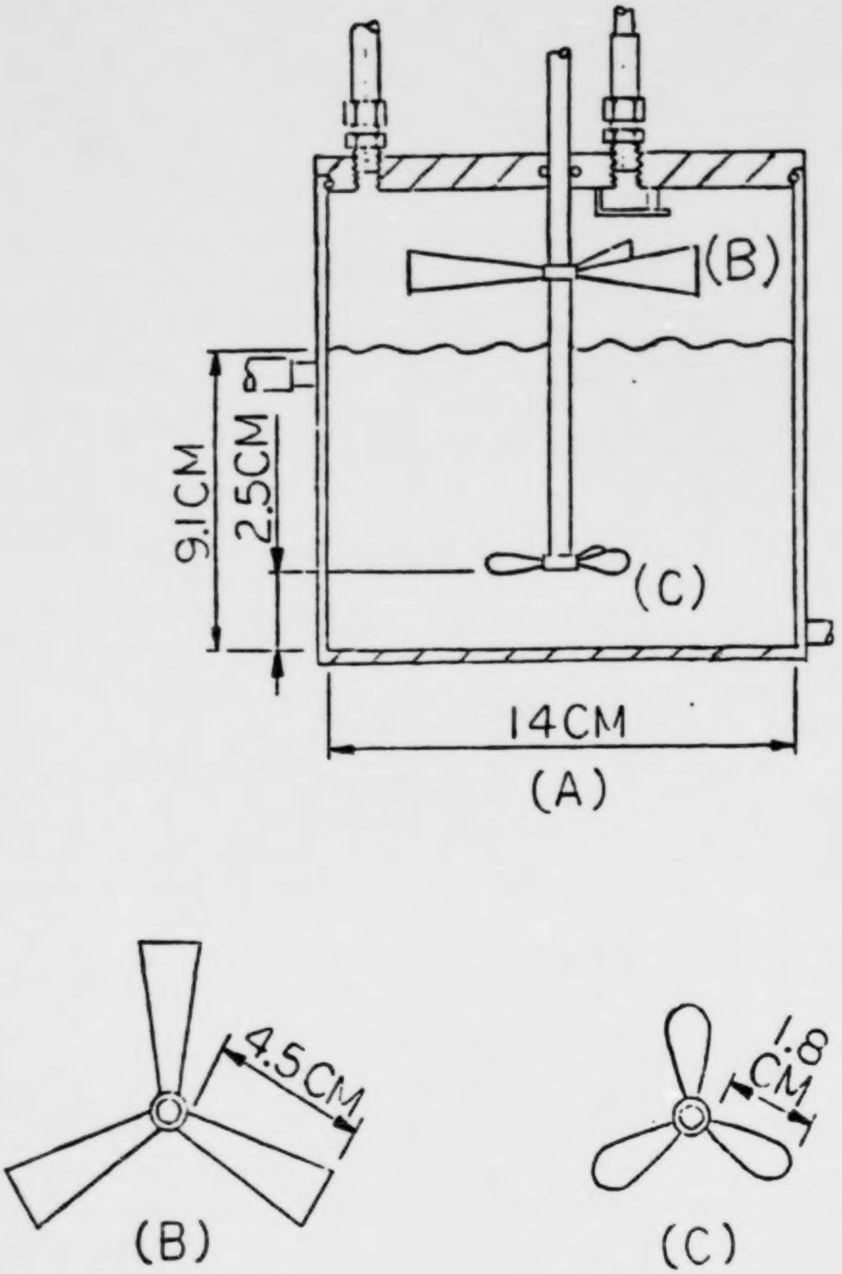

(B)
9.1CM
2.5CM
(C)
14CM
(A)
4.5CM
(B)
1.8 CM
(C)

Figure 2-6. Reaction Vessel and Agitators

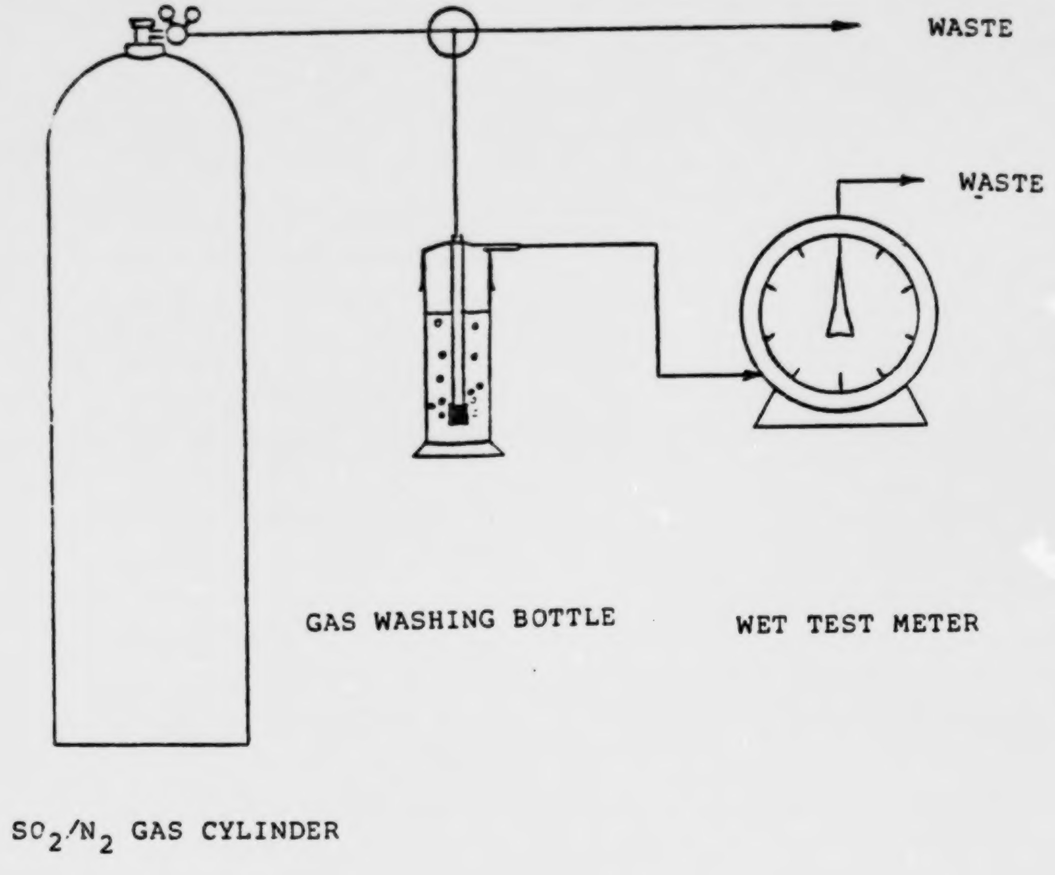

WASTE
WASTE
GAS WASHING BOTTLE
WET TEST METER
SO_2/N_2 GAS CYLINDER

Figure 2-7. Dynamic Saturation Apparatus

MATERIAL BALANCES

The sulfur dioxide absorption rate was calculated from a material balance based on the gas flow rate and the SO_2 concentration in the inlet and outlet gases. In early characterization experiments, the overall material balance was checked by an analysis of the liquid phase with iodimetric titration and with ion chromatography. The results agreed within 10%.

An ion chromatograph was used to determine the total sulfur content of the liquid streams. The solution was treated with hydrogen peroxide to oxidize the sulfite to sulfate. Total sulfate was then determined by a Dionex Model 14 Ion Chromatograph.

Iodimetric titration was also used to determine the sulfite content of the liquid streams in and out. Excess iodine was added to a known volume of sample liquid. This sample was then titrated to a starch endpoint using sodium thiosulfate, $Na_2S_2O_3$.

SYSTEM CHARACTERIZATION

The experimental apparatus was characterized and the experimental error checked by sulfur dioxide absorption into NaOH and HCl solutions.

Sodium Hydroxide

Concentrated sodium hydroxide absorption experiments were designed to measure the gas phase resistance to mass transfer. The key assumption was that instantaneous irreversible neutralization of sulfur dioxide occurred in the presence of excess hydroxide at the gas-liquid interface. This assumption was based on the reaction

$$2\ OH^- + SO_2 \rightleftharpoons SO_3^= + H_2O \qquad 2\text{-}3$$

In the presence of enough hydroxide this reaction eliminated the liquid phase resistance to sulfur dioxide transfer. Therefore, the mass transfer coefficient derived from the experimental data measured only the gas phase resistance. Preliminary tests established that 0.3 M NaOH was sufficiently concentrated to eliminate liquid-phase resistance.

In the apparatus the gas phase mass transfer coefficient was found to be a function of agitator speed, Figures 2-8. Two distinct agitation zones were observed. Below 650 rpm there was a smooth, unbroken gas-liquid interface.

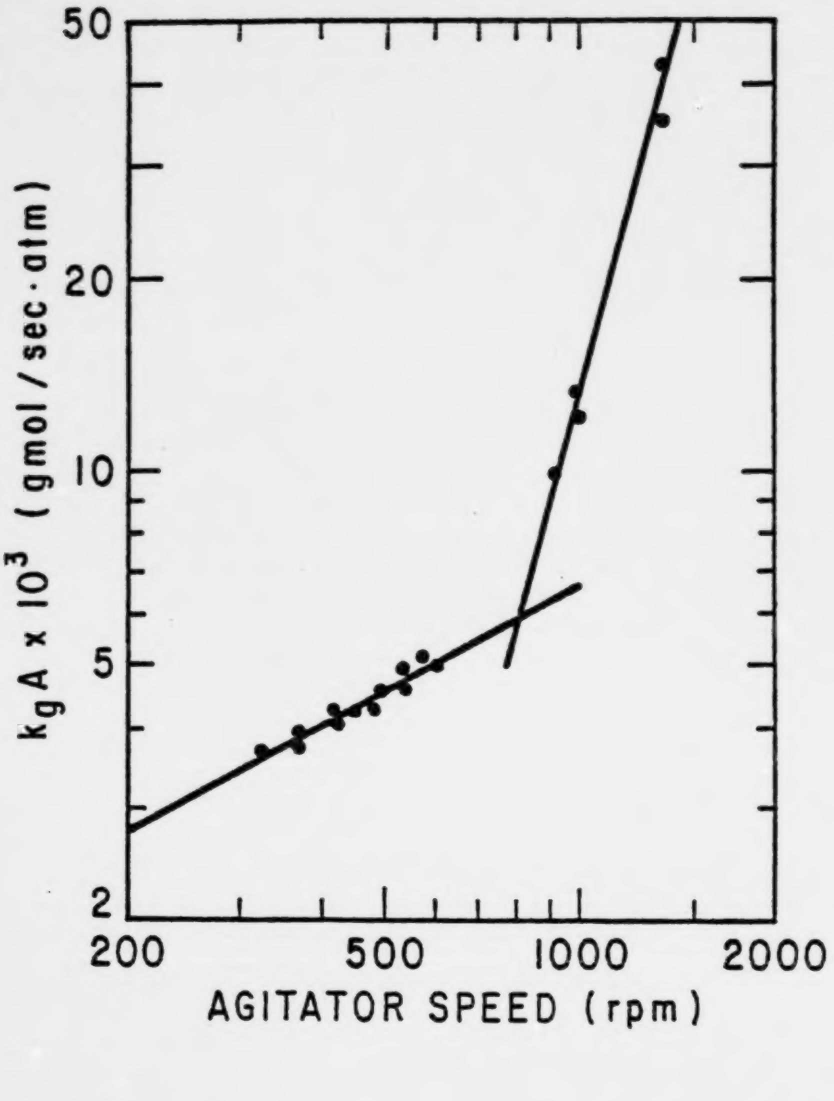


Figure 2-8. Gas Phase Mass Transfer Coefficient as a Function of Agitation Rate, 0.3 M NaOH, 55°C

In this zone k_gA increased with agitation rate to the 0.6 power. Above 650 rpm the interface was broken by gas bubbles being sucked into the liquid. In this zone the increasing gas-liquid contact area resulted in a k_gA dependence on the 3.6 power of agitator speed. Due to problems of characterization and reproducibility all subsequent experiments were run at 540 rpm with a smooth, unbroken gas-liquid interface. The k_gA value at 55°C was found to be 4.93×10^{-3} gmol/atm.sec at 2700 ppm sulfur dioxide.

Hydrochloric Acid

Concentrated hydrochloric acid experiments were performed to determine the liquid phase mass transfer in the absence of chemical reactions. All subsequent experimental enhancement factors at higher pH values were calculated relative to this case of physical absorption. Preliminary experiments established that 0.3 M HCl was adequate to suppress the enhancement of sulfur dioxide absorption by the hydrolysis reaction, Reaction 2.2. At 540 rpm and 55°C the liquid phase mass transfer coefficient, $k_1^\circ A$, was 1.5×10^{-3} l/sec with 2000 ppm SO_2 in the gas phase. Under these conditions the SO_2 concentration at the gas-liquid interface was 1600 ppm.

In subsequent experiments at higher pH, the interfacial SO_2 partial pressure ($P_{SO_{2,i}}$) was calculated from the absorption rate (N):

$$P_{SO_{2,i}} = P_{SO_2} - N/k_gA \qquad 2\text{-}43$$

Equilibrium at the gas-liquid interface is given by Henry's law:

$$[SO_2]_i = P_{SO_{2,i}}/H \qquad 2\text{-}44$$

The enhancement factor, ϕ, was calculated from the equations:

$$k_1A = N/([SO_2]_i - [SO_2]) \qquad 2\text{-}45$$

$$\phi = k_1A/k_1^\circ A \qquad 2\text{-}46$$

BUFFER PREPARATION

All experiments used reagent grade buffers except for the three cases cited below. In these three cases the laboratory techniques developed by Smith (1981) and Cavanaugh (1978) were used to synthesize the buffers.

B-Hydroxypropionic Acid

B-hydroxypropionic acid was prepared by hydrating reagent grade acrylic acid with acid catalysis:

$$CH_2{=}CH{-}COOH + H_2O \rightarrow HOCH_2{-}CH_2{-}COOH \qquad 2\text{-}47$$

A 2.0 molar acrylic acid solution was reacted in the presence of 1.5 M H_2SO_4 at 105°C for over 13 hours. A conversion of 85-95% was determined using ion chromatography.

Sulfopropionic Acid

Acrylic acid was sulfonated with sodium sulfite to sulfopropionic acid

$$CH_2{=}CH{-}COOH + SO_3^{=} \rightarrow SO_3^{-}CH_2{-}CH_2{-}COO^{-} \qquad 2\text{-}48$$

Ninety-eight percent conversion was achieved by reacting one mole of reagent grade acrylic acid with one mole of reagent grade sodium sulfite in one liter of water. A constant temperature bath was used to hold the reacting mixture at 55°C for 10 hours. The conversion was determined by iodimetric titration for sulfite in the final solution.

Sulfosuccinic Acid

Maleic acid was sulfonated in the presence of sodium sulfite to form sulfosuccinic acid:

$$HOOC{-}CH{=}CH{-}COOH + HSO_3^{-} \rightarrow HOOC{-}SO_3^{-}CH{-}CH_2{-}COOH \qquad 2\text{-}49$$

Sulfosuccinic acid was prepared in the same fashion as sulfopropionic acid. One mole of reagent grade maleic acid was added to one mole of dissolved soium sulfite in one liter of water at 55°C for 12 hours. This resulted in 95% conversion as determined by iodimetric titration.

CHAPTER 2-4

RESULTS AND DISCUSSION

The experiments were performed with two primary objectives: 1) to quantify the effects of buffer and alkali additives on sulfur dioxide mass transfer, and 2) to validate the model of mass transfer with equilibrium reactions at 55°C and in solutions containing magnesium and calcium. Sulfur dioxide absorption rates were measured in systems containing sulfite and sulfate, and in systems containing buffers. These experimental results were combined with measurements of gas- and liquid-side mass transfer coefficients in the absence of chemical reaction (Chapter 2-3) to develop enhancement factors for liquid-side mass transfer coefficients with chemical reactions.

Measurements were made in systems involving sulfite and sulfate because they are simple from a modeling viewpoint and because the results are applicable to the analysis of alkali additives. These experiments were performed in systems containing: 1) sulfite, 2) sulfate, and 3) sulfite/bisulfite. The sulfite experiment was undertaken as the simplest system in terms of modeling that would yield information on alkali additives and hydrolysis. Sulfate experiments added some complexity to the sulfite system, for modeling, and gave information on forced oxidation. The sulfite/bisulfite interaction tested the model at lower pH while giving absorption rate results under conditions typically found in a scrubber, both with and without alkali additives.

Systems involving buffers were investigated to determine their applicability to $CaO/CaCO_3$ slurry scrubbing. The information sought in these experiments was the sulfur dioxide absorption rate as a function of buffer concentration. This information is used to evaluate the buffers in terms of mass transfer and cost effectiveness. The buffers used were those which appeared to have the best mass transfer characteristics as evaluated by Chang (1979) at 25°C in NaCl solutions. This work provides data on the buffers at 55°C in solutions containing sodium and calcium.

SULFITE, SULFATE, AND ALKALI ADDITIVES

Sulfite

Experiments were run to determine the effects of sulfite concentration and sulfur dioxide partial pressure on the enhancement factor in 0.3 M NaCl and 0.1 M $MgCl_2$. The experiments were performed at 55°C and pH 8.5 with sulfite concentrations varied between 2 and 14 mM.

Figure 2-9 is a parity plot comparing the experimental results for absorption of dilute SO_2 into 0.3 M NaCl with the results predicted by the enhancement factor model, Eq. 2-31. The results show agreement within 15%, comparable to the experimental error observed in the characterization experiments.

The enhancement factor model was used to develop Figures 2-10 which shows the effect of sulfite concentration on sulfur dioxide absorption. At low $[SO_2]/p_{SO_2}$ the enhancement is a strong function of SO_2 partial pressure, while at high $[SO_2]/p_{SO_2}$ it is independent of p_{SO_2}. This demonstrates the importance of the hydrolysis reaction at low $[SO_2]/p_{SO_2}$.

The sulfur dioxide absorption rate was also measured in 0.1 M $MgCl_2$ solution. In this case the enhancement factor results were fitted to the experimental data, to account for the magnesium ion pairing, by adjusting the sulfite and bisulfite diffusivities. The sulfite and bisulfite diffusivities were reduced 45% and 25%, respectively, from their values in an infinitely dilute solution. Figure 2-11 is a parity plot showing the results with adjusted diffusivities. The enhancement factor model is used in Figure 2-12 to illustrate the effect of increased sulfite concentration on the enhancement factor.

The ion pairing effect on sulfur dioxide absorption in sulfite solutions at 55°C, 0.3 M total ionic strength, pH 8.5, and 1000 ppm SO_2 is illustrated in Figure 2-13, where the model was used to compare absorption in 0.1 M $MgCl_2$ and in 0.3 M NaCl. The enhancement reduction due to ion pairing is more dramatic at high sulfite concentrations where sulfite diffusion controls the absorption rate. At these high sulfite concentrations the enhancement in NaCl solutions is as much as 25% higher than in $MgCl_2$ solutions.

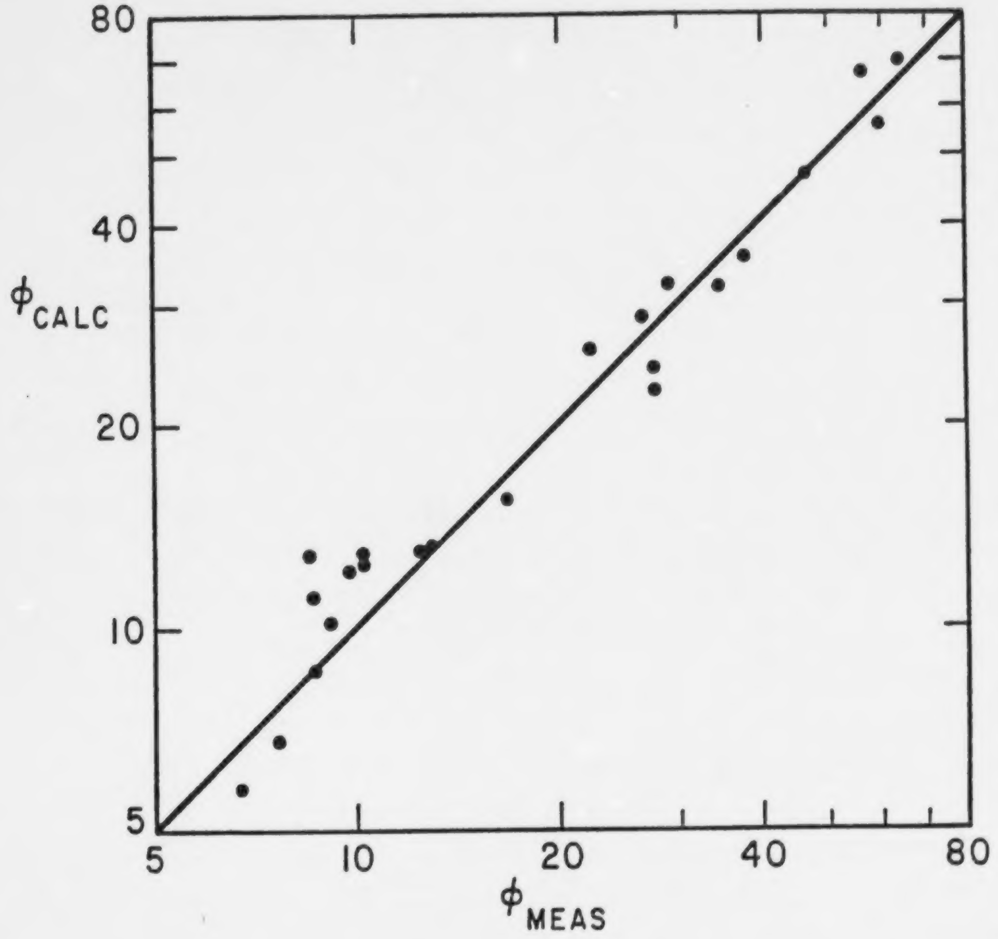


Figure 2-9. Parity Plot for SO_2 Absorption in 0.3 M NaCl at 55°C and pH 6.5, with 2 to 20 mM Na_2SO_3

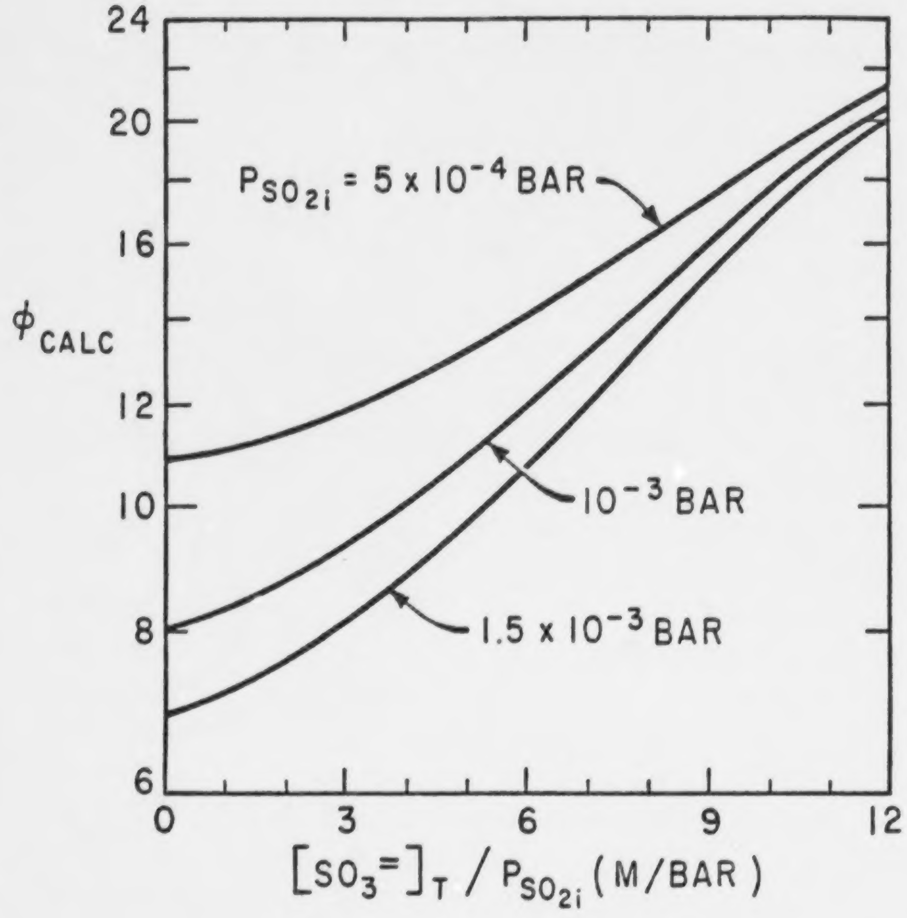


Figure 2-10. Effect of Sulfite in 0.3 M NaCl at 55°C, pH 8.5

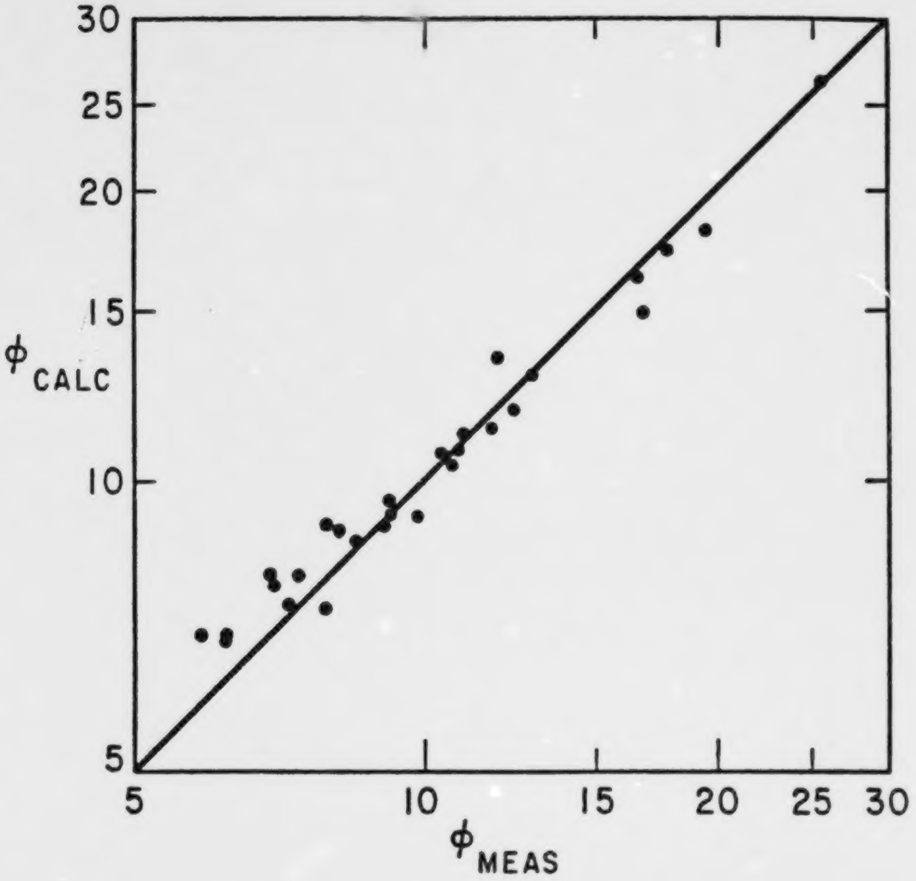


Figure 2-11. Parity Plot for SO_2 Absorption in 0.1 M $MgCl_2$ at 55°C and pH 8.5 with 2 to 20 mM Na_2SO_3

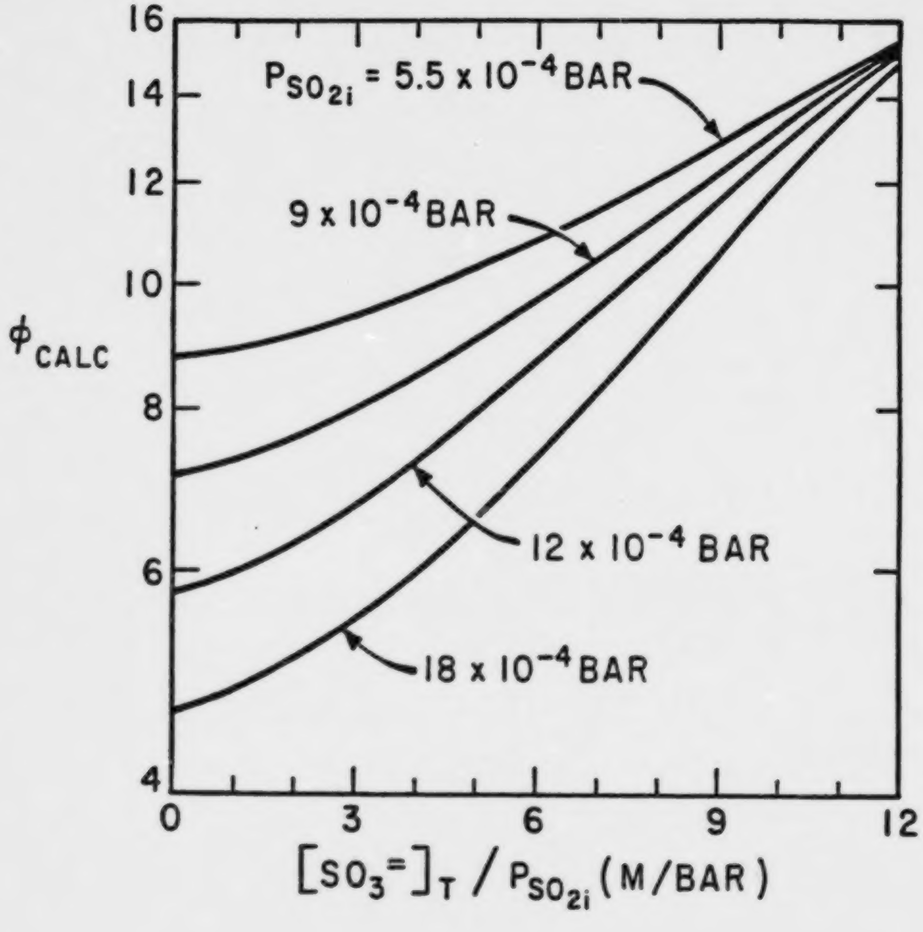


Figure 2-12. Effect of Sulfite in 0.1 M $MgCl_2$

at 55°C and pH 8.5

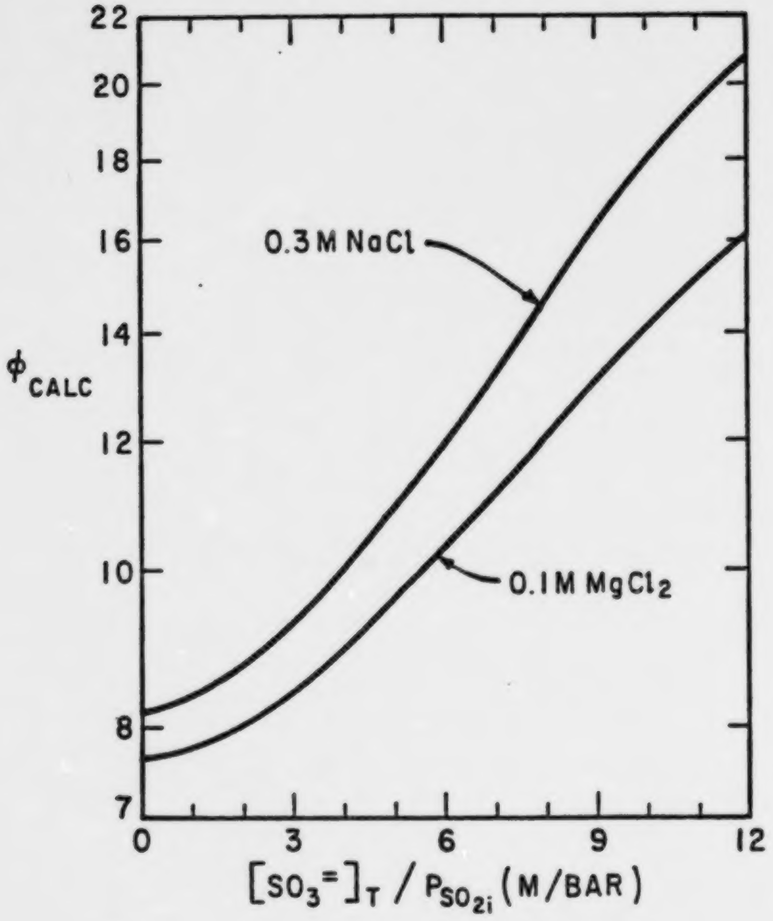


Figure 2-13. Ion Pairing Effect in 0.3 M Ionic Strength

Solutions at 55°C and pH 8.5

Sulfate

The sulfate experiments were used to determine both concentration effects and buffering effectiveness of the sulfate with alkali additives.

The effect of dissolved sulfate on sulfur dioxide absorption is presented in Figure 2-14. The observed effects can be explained as changes in ionic strength and buffer capacity. At low ionic strength electric potential gradients have a significant effect on the diffusivity and on the activity coefficients of the ions, thus on the apparent equilibrium constants. These effects give the rapid initial increase in the enhancement factor.

The buffering effect was observed at higher ionic strengths where the diffusivities and pK_a values have stabilized. At sulfate concentrations greater than 0.2 M the reaction

$$SO_4^{=} + SO_2 + H_2O \rightleftharpoons HSO_4^- + HSO_3^-$$

provides an enhancement that increases slowly with sulfate addition.

Ion pairing was also demonstrated in this set of experiments. Bivalent magnesium ions interacted with and reduced the diffusivity of sulfate, as well as sulfite, 45%, which in turn reduced the enhancement in the presence of bivalent cations.

Figure 2-15 illustrates experimental work over a 2-12 mM total sulfite range at 55°C, pH 8.5, 1250 ppm SO_2, in 0.1 M Na_2SO_4 and in 0.1 M $MgSO_4$. In modeling the magnesium sulfate system the univalent and bivalent anion diffusivities were reduced by 25 and 45%, respectively.

The enhancement model was used to produce Figure 2-16 at 1250 ppm SO_2, pH 8.5, and 55°C to demonstrate the effect of sulfite in the presence of sulfate. This figure reiterates the reduction in enhancement with bivalent cations in solution. In this case the bivalent cation depresses the enhancement by approximately 20%.

The increased enhancement in sulfate solutions can be seen by comparing Figures 2-13 and 2-16 at the same sulfite concentration. This shows that at low sulfite concentrations there is a 35% increase in enhancement with the sulfate model. However, as the sulfite concentration increases, the sulfite becomes a more influential factor in the absorption, resulting in enhancement factors that are relatively independent of sulfate.

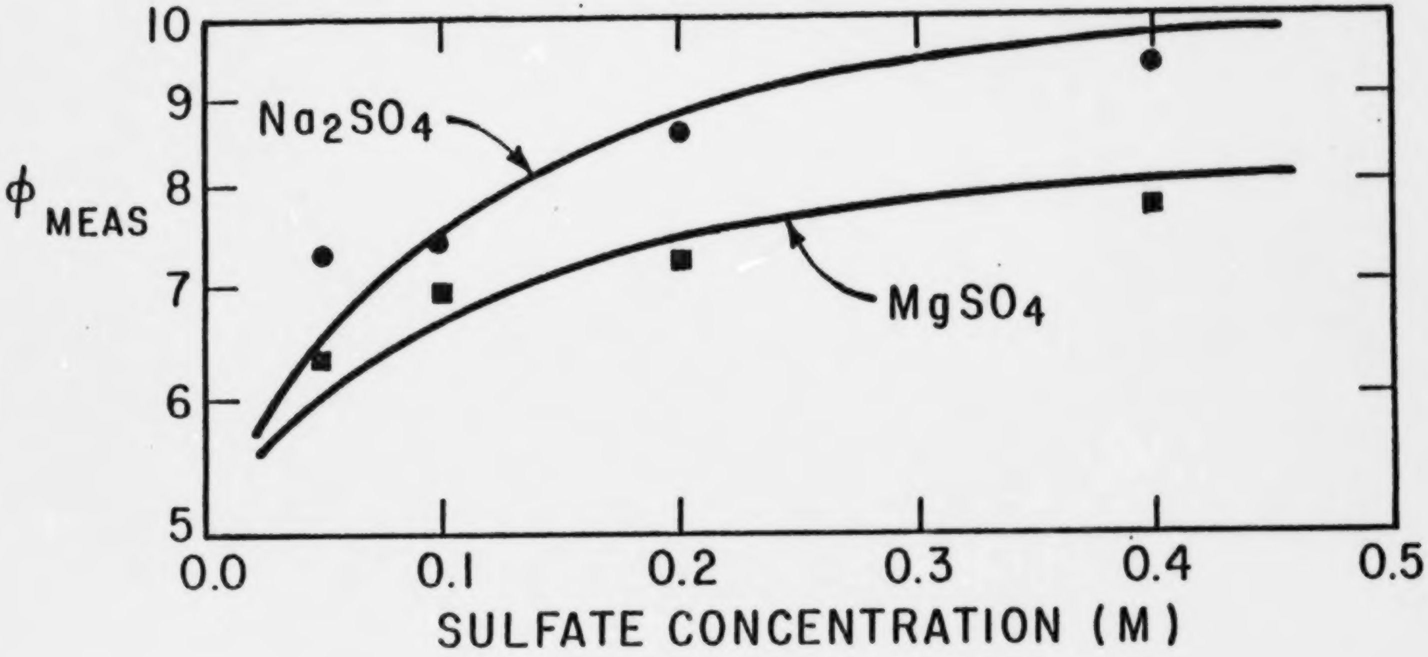


Figure 2-14. Effect of Sulfate on SO_2 Absorption at 55°C, pH 4.6, 1250 ppm SO_{2i}

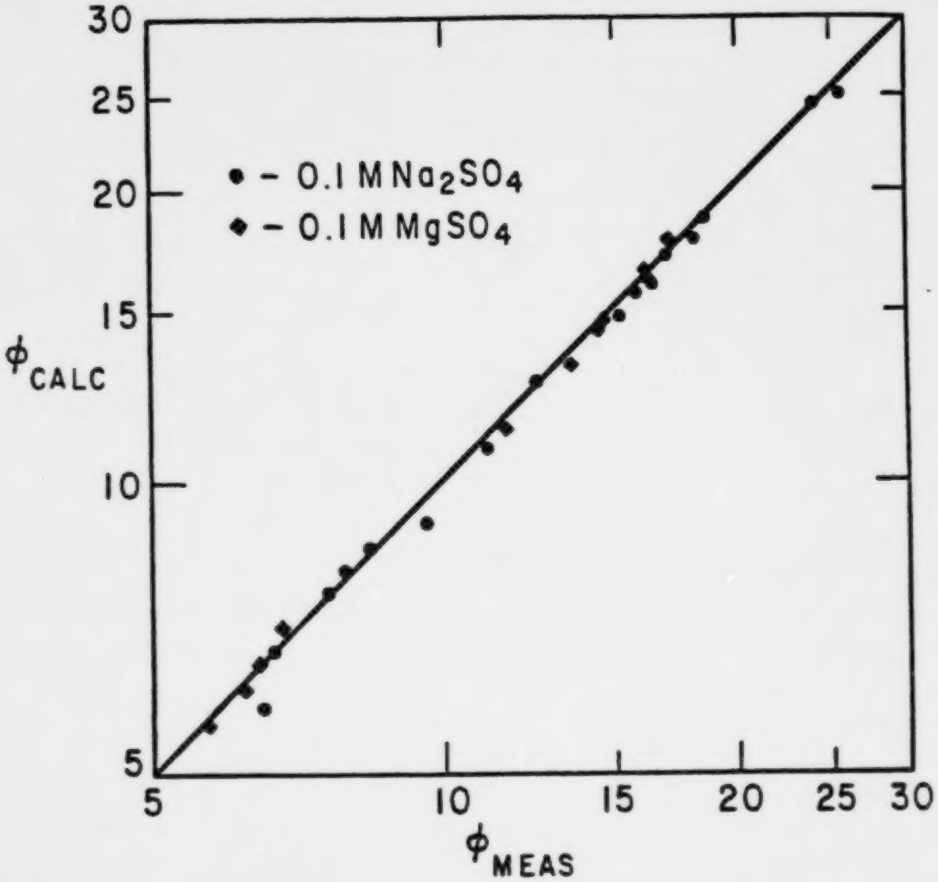


Figure 2-15. Parity Plot for 0.1 M Sulfate Solutions

at 55°C, pH 8.5, and 1000 ppm SO_{2i}, with 2 to 12 mM Total Sulfite

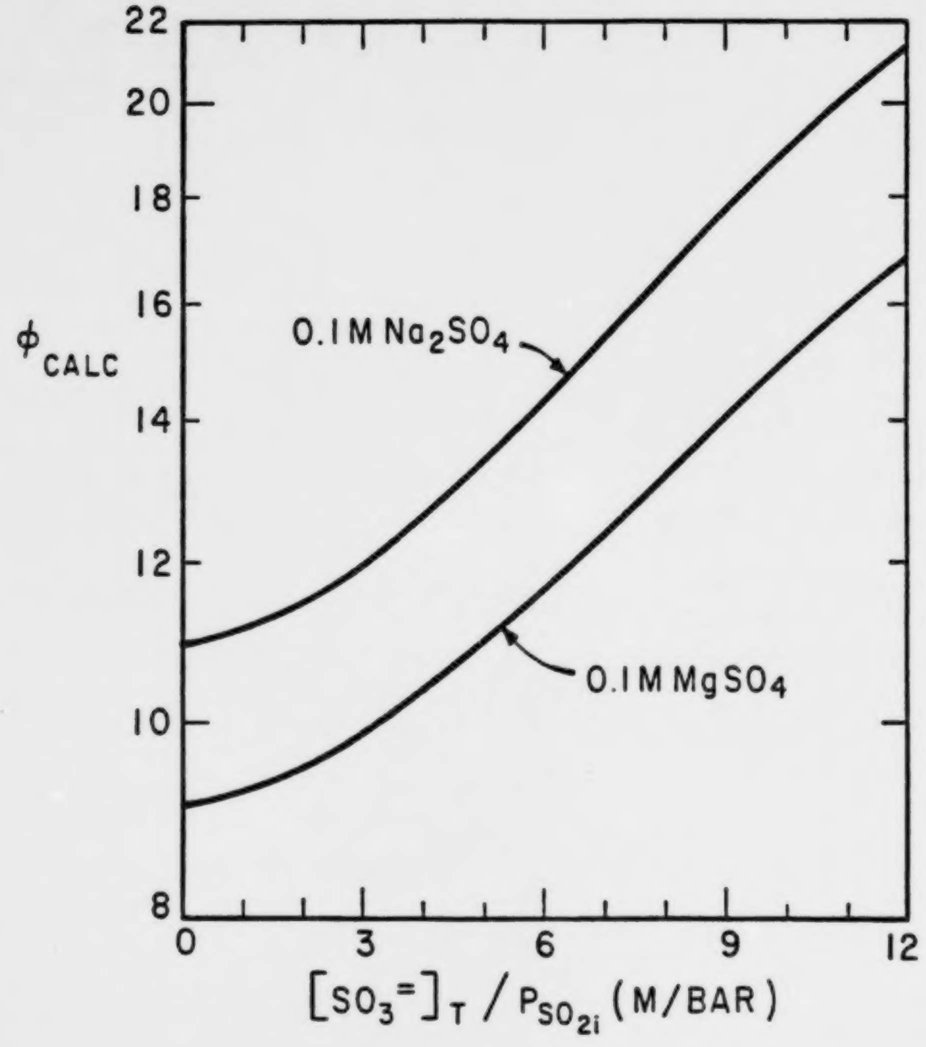


Figure 2-16. Effect of Sulfite in Sulfate Solutions

at 55°C pH 8.5, and 1000 ppm SO_{2i}

Sulfite/Bisulfite

The effects of the sulfite/bisulfite interaction were observed at conditions which simulated actual SO_2 scrubbing. These experiments were performed to quantify the bisulfite suppression of sulfur dioxide mass transfer with increasing sulfite concentration.

The experiments were performed in NaCl, $CaCl_2$, and $MgCl_2$ solutions at 55°C, 0.3 M total ionic strength, pH 4.5, and 1000 ppm SO_2 with the total sulfite concentration varied between 2 and 40 mM. The sulfite/bisulfite experimental results agree well with the equilibrium model results, Figure 2-17, after correcting for the bivalent cations by reducing uni- and bivalent anion diffusivities by 25 and 45%, respectively, in solutions of $MgCl_2$ and $CaCl_2$.

Figure 2-18 uses the enhancement model to predict the effects of calcium, magnesium, and sodium ions on the sulfite/bisulfite interactions from 0 to 40 mM total sulfite at the experimental conditions. The figure demonstrates the effects of the hydrolysis reaction on sulfur dioxide mass transfer. At low sulfite an increase in total sulfite concentration suppresses the hydrolysis reaction. As the sulfite concentration increases further, Reaction 2-2 starts to play a more important role; the sulfite reacts with sulfur dioxide to form bisulfite, thus enhancing SO_2 absorption. The sulfite enhancing effect gradually increases in dominance until finally controlling mass transfer, leading to the gradual increase in enhancement with $[SO_2]/p_{SO_2}$ greater than 20.

After accounting for ion pairing, by reducing the uni- and bivalent anion diffusivities by 25 and 45% in both the $MgCl_2$ and $CaCl_2$ solutions, the enhancement of all three solutions is approximately equal. This is due to more favorable equilibrium constants in $CaCl_2$ and $MgCl_2$. The equilibrium constants in solutions containing magnesium and calcium give higher sulfite and, therefore, improve enhancement.

The minimum in the enhancement factor curve shows that an increase of total sulfite can reduce the liquid phase mass transfer coefficient by as much as 50%, in this pH range.

BUFFER ADDITIVES

Six buffers were chosen for in-depth mass transfer analysis: acetic,

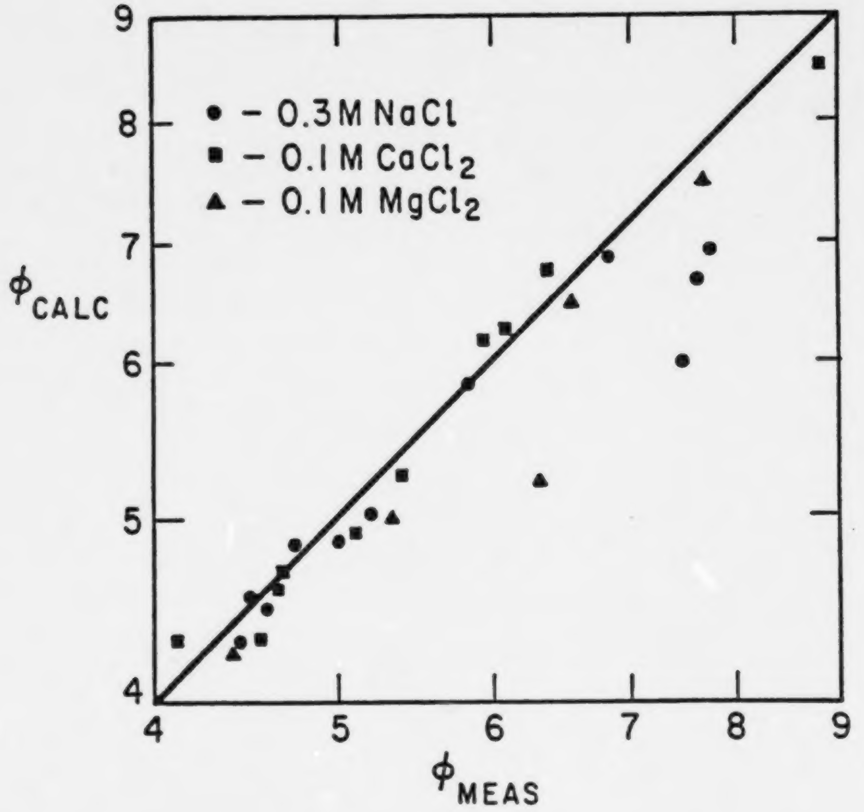


Figure 2-17. Parity Plot for Chloride Solutions at 55°C, pH 4.5, and 1000 ppm SO_{2i} with 3 to 17 mM Total Sulfite

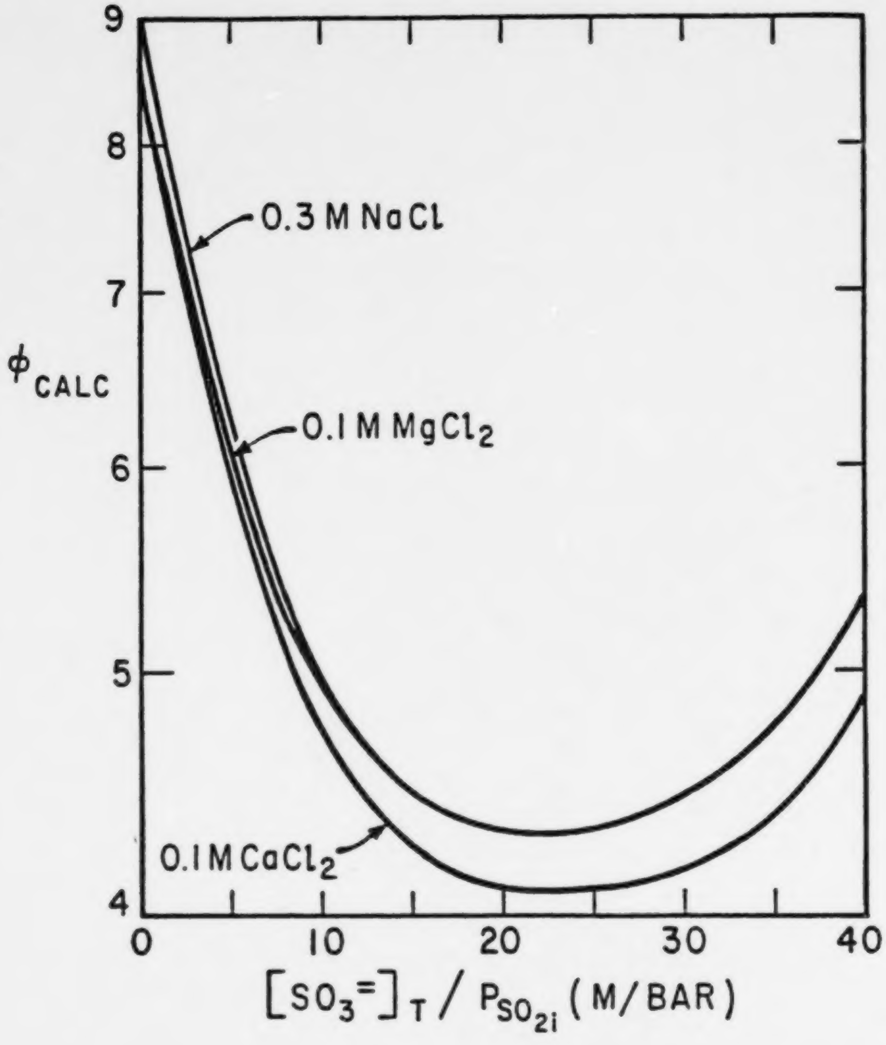


Figure 2-18. Effect of Sulfite in Chloride Solutions at 55°C, pH 4.5, and 1000 ppm SO_{2i}

adipic, hydroxypropionic, sulfopropionic, and sulfosuccinic acids and aluminum chloride. These six were chosen to represent industrially applicable buffer additives. The experimental results of these buffers were combined with the enhancement factor model to evaluate the economic feasibility of the buffers.

The absorption of sulfur dioxide into aqueous buffered solutions employed the same experimental apparatus and techniques used with non-buffered solutions. The enhancement factor equation was used to model the experimental data. The equilibrium constants used in the model were taken from Cavanaugh (1978) and Chang (1979), Tables 2-2 and 2-3, while estimated diffusivities were taken from Chang (1979) and adjusted to fit the experimental results, Table 2-3. Where bivalent cations were used in the bulk solution, the anion diffusivity values were reduced to account for ion pairing. The reductions were 25 and 45% for uni- and bivalent anions, respectively.

All carboxylic acid experiments were run at 55°C, pH 5.5, 1000 ppm interfacial gas phase sulfur dioxide concentration, and 3 to 5 mM total sulfite in 0.3 M ionic strength solutions (0.3 M NaCl or 0.1 M $CaCl_2$), except for adipic acid which was also run at pH 4.2. The only experimental parameter changed was the buffer concentration which was varied between 0 and 20 mM. The experimental results of all carboxylic acids are compared with the results predicted by the model in Figure 2-19. The only diffusivity value that deviated from the value predicted by Chang was that of sulfopropionic acid which experimentally was 0.4 cm^2/sec, instead of 0.8 cm^2/sec in theory.

The graphs for specific buffers (Figures 2-20 to 2-24) were developed using the enhancement factor model to show the effect of buffer concentration. The model parameters were set at 55°C, pH 5.5, 30 mM total sulfite, and 1000 ppm interfacial sulfur dioxide partial pressure in 0.3 M total ionic strength solutions, either 0.3 M NaCl or 0.1 M $CaCl_2$. The enhancement factor is plotted versus the ratio of the basic buffer species to the sulfur dioxide partial pressure to reduce the dependence of the results on pH and p_{SO_2}. All of the results show the strong effects of buffer concentration and the reduced enhancement factors in $CaCl_2$ solutions, Figure 2-20, especially with polyfunctional buffers.

Acetic acid was investigated to typify the effect of a monofunctional buffer on absorption rate, Figure 2-20. Chemical Construction Co. has patented the use of acetic acid, along with formic and propionic acids.

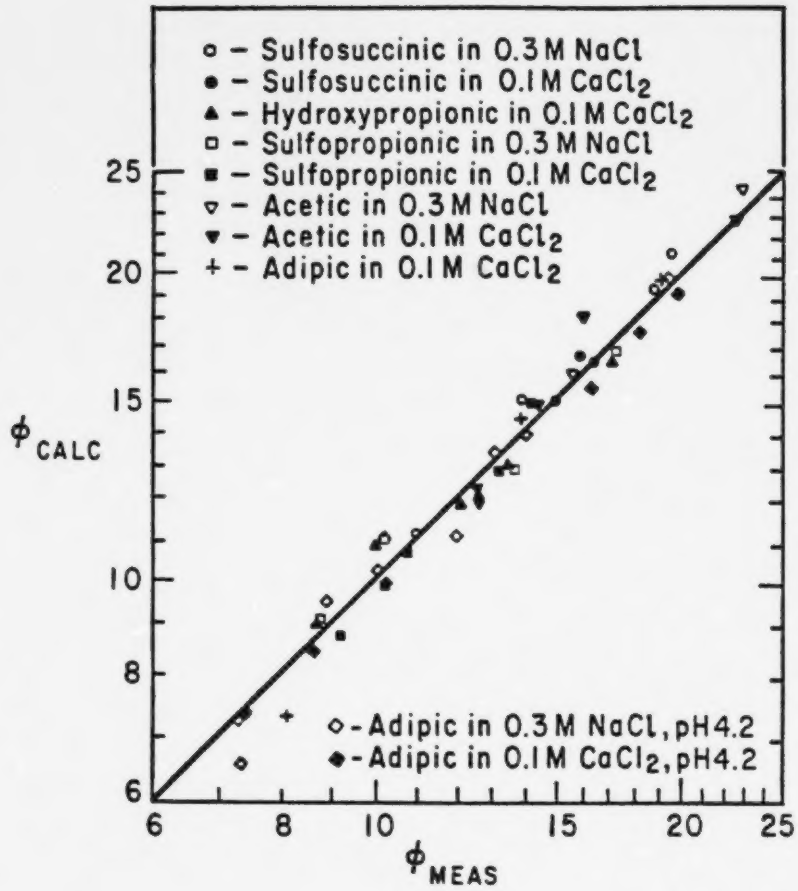


Figure 2-19. Parity Plot for Buffer Additives in 0.3 M Ionic Strength Solutions at 55°C, pH 5.5, and 1000 ppm SO_{2i}

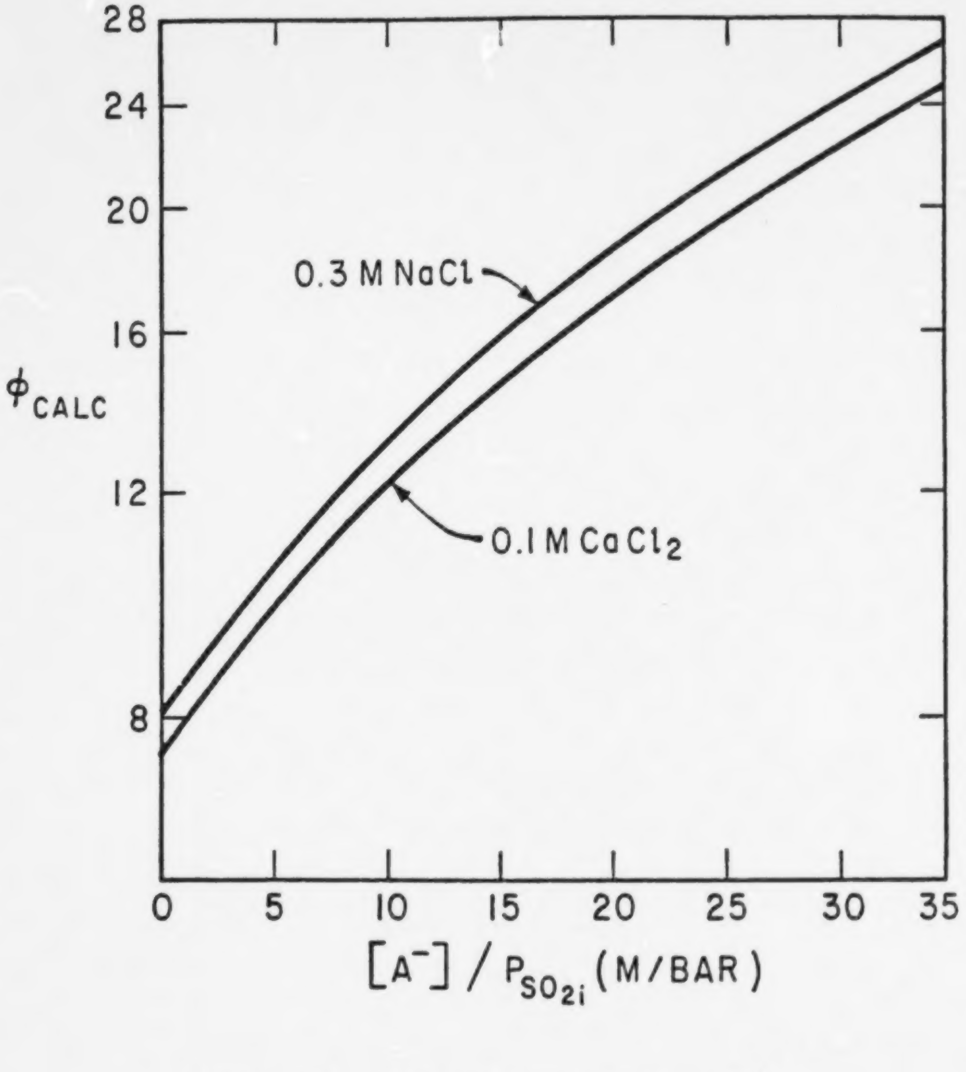


Figure 2-20. Effect of Acetic Acid at 55°C,

pH 5.5, 3 mM Total Sulfite, and 1000 ppm SO_{2i}

Acetic acid proved to have good absorption rate characteristics.

Adipic acid was used to typify bifunctional buffers. Figure 2-21 quantifies the effect of adipic acid addition. The graph emphasizes that with bifunctional buffers the ion pairing effect becomes larger at higher acid concentrations, resulting in an increasing relative difference between the univalent and bivalent cation cases.

Hydroxypropionic acid is synthesized by hydration of acrylic acid, making it relatively nonvolatile because it has two hydrophylic groups. Only a calcium based model was run with this buffer, Figure 2-22, but these results proved it had good enhancing capabilities. The model was also used in combination with the experimental data to show that the buffer acted like a monofunctional buffer, requiring only a 25% reduction in the diffusivity of its fully dissociated anion.

Sulfopropionic acid, synthesized by sulfite addition to acrylic acid, acts like a monofunctional buffer. In this case the sulfonic acid group is a strong acid making the buffer nonvolatile at scrubbing conditions, while the carboxylic acid group is the effective buffer. Enhancement is not as good as expected, giving low apparent diffusivity, 0.4×10^{-5} cm^2/sec versus $0.8\text{-}0.9\times10^{-5}$ cm^2/sec expected. The unexpectedly low diffusivity may be caused by polymerization of the acrylic acid during synthesis.

Sulfosuccinic acid, produced by reacting sulfite with maleic anhydride, is a trifunctional acid which acts like a bifunctional acid for absorption rate enhancement. The enhancement model, Figure 2-24, shows sulfosuccinic acid to be a good enhancer and, once again, illustrates the relative reduction in enhancement increases with higher buffer concentrations in the presence of calcium.

The model was used (at 55°C, pH 5.5, 1000 ppm sulfur dioxide interfacial concentration, 3.0 mM total sulfite, and 0.3 M $CaCl_2$) to compare the effectiveness of the buffers examined in this section, Figure 2-25. The graph clearly demonstrates that adipic acid is the most effective buffer, on a concentration basis, followed by sulfosuccinic, acetic, hydroxypropionic, and sulfopropionic, in that order. The graph also clearly demonstrates the detrimental effect of the low diffusivity associated with sulfopropionic acid.

Aluminum chloride is separated from the organic buffers due to the unpredicted results obtained. Aluminum chloride was the only inorganic

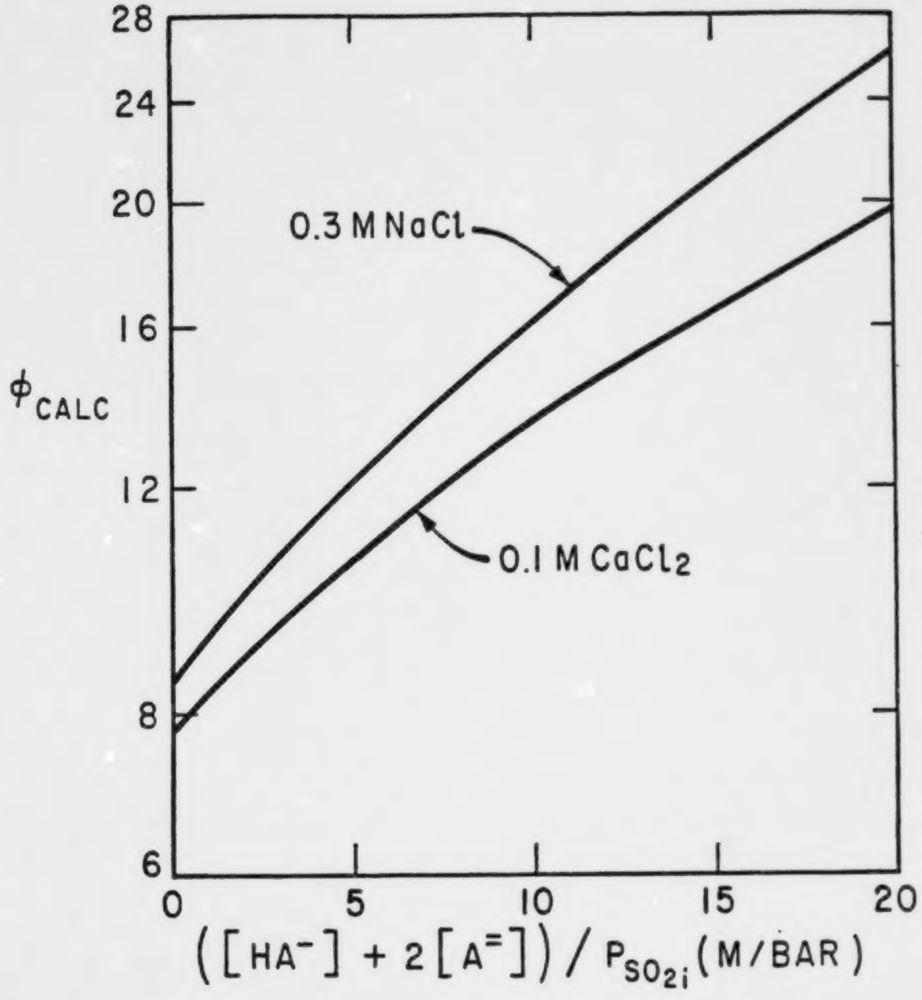


Figure 2-21. Effect of Adipic Acid at 55°C,

pH 5.5, 3 mM Total Sulfite, and 1000 ppm SO_{2i}

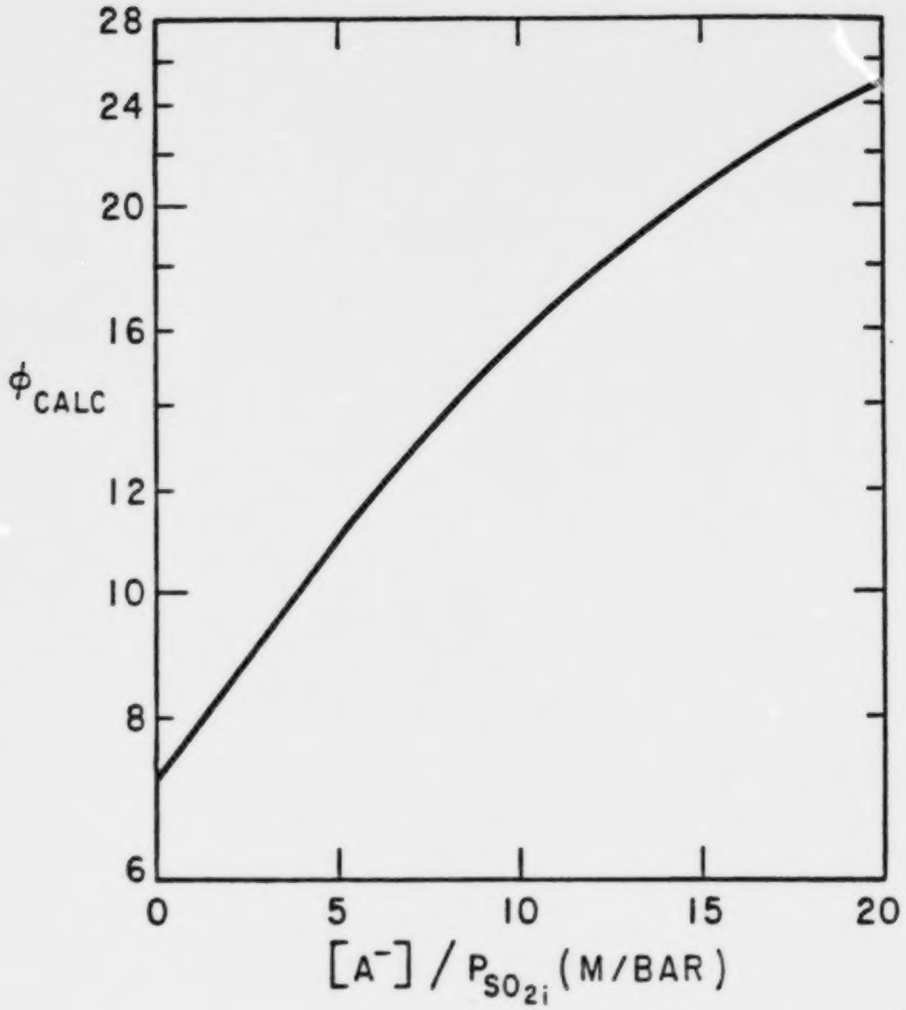


Figure 2-22. Effect of Hydroxypropionic Acid in 0.1 M $CaCl_2$ Solutions at 55°C, pH 5.5, 3 mM Total Sulfite, and 1000 ppm SO_{2i}

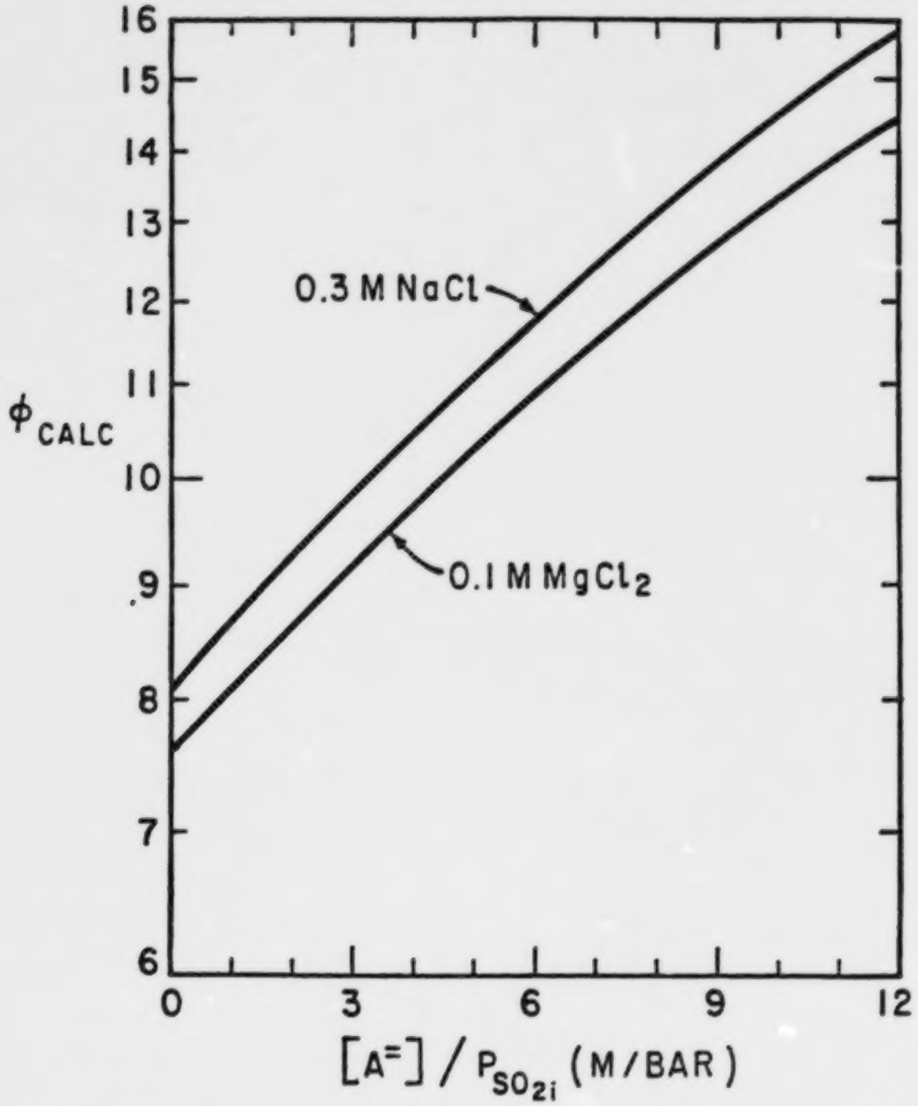


Figure 2-23. Effect of Sulfopropionic Acid

at 55°C, pH 5.5, 3 mM Total Sulfite, and 1000ppm SO_{2i}

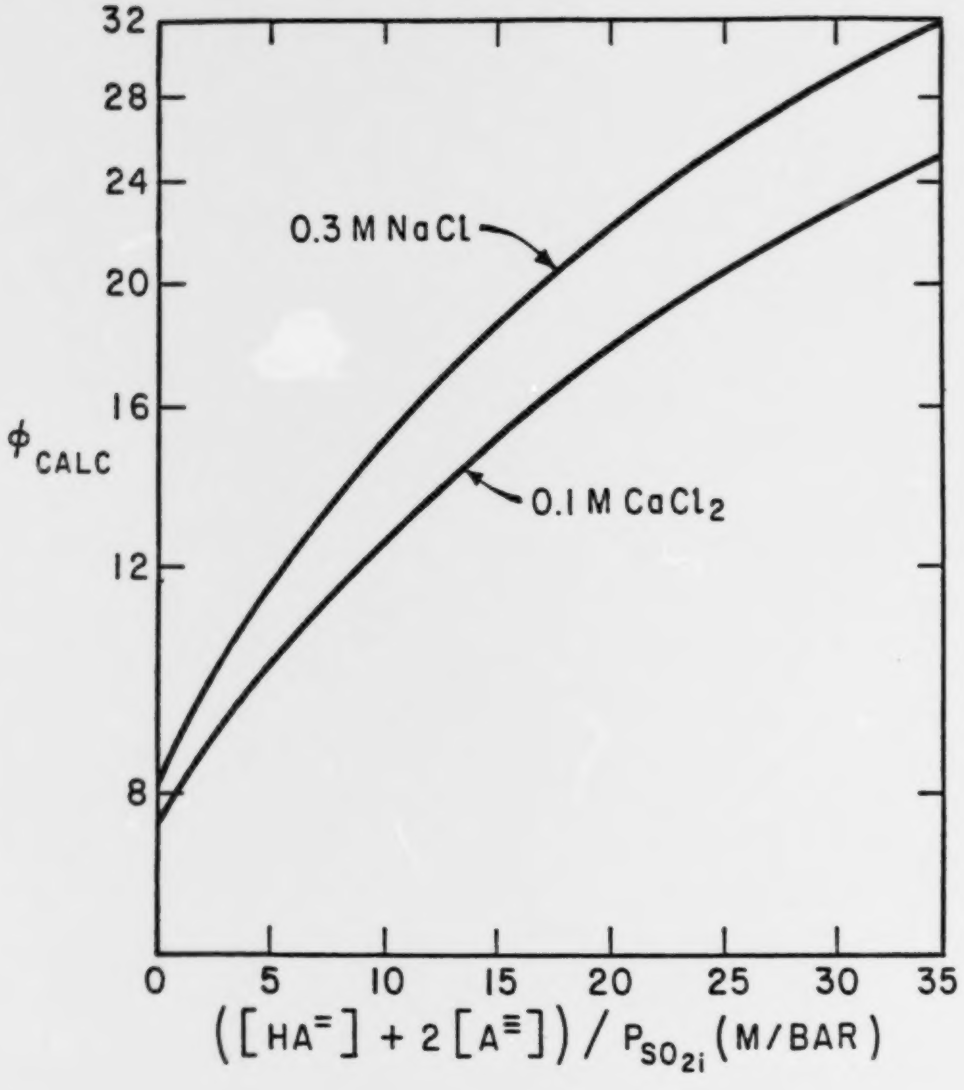


Figure 2-24. Effect of Sulfosuccinic Acid at 55°C

pH 5.5, 3 mM Total Sulfite, and 1000 ppm SO_{2i}

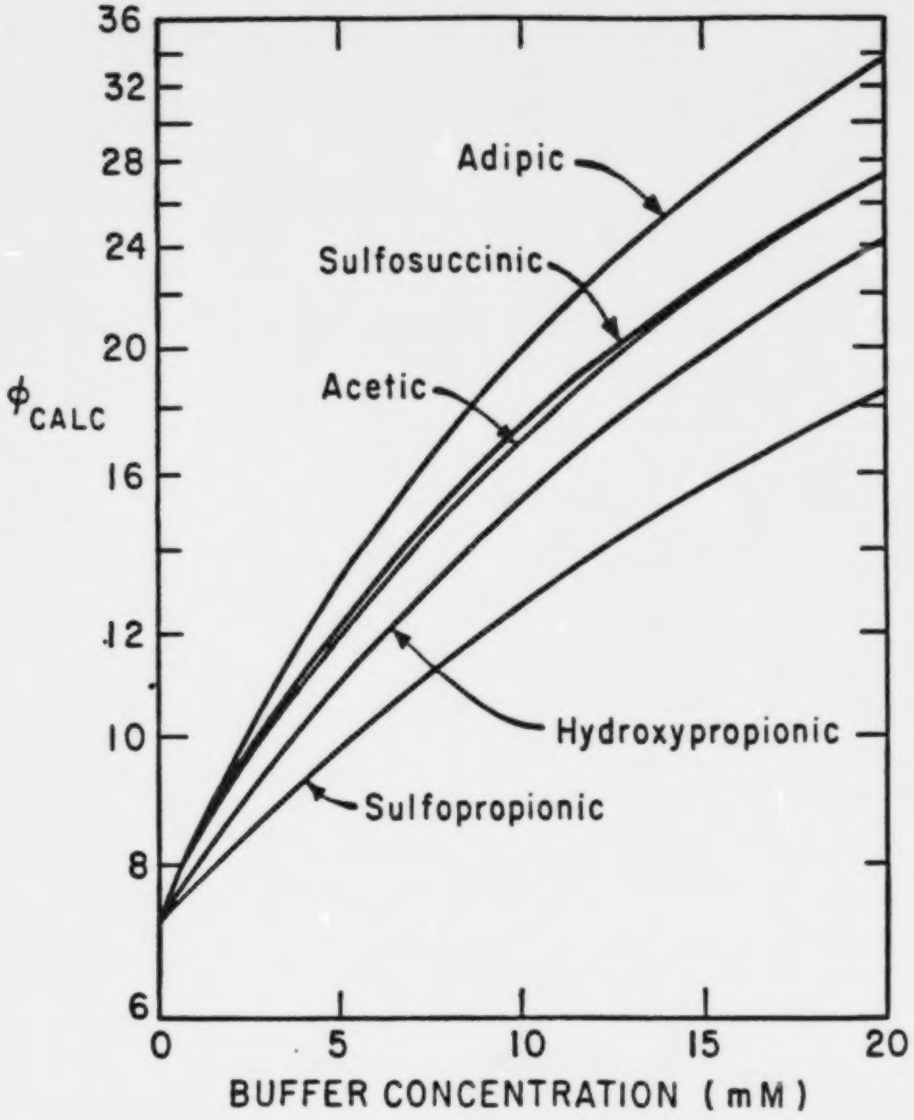


Figure 2-25. Effect of Alternative Buffers in

0.1 M $CaCl_2$ at 55°C pH 5.5, 3 mM Total Sulfite, and 1000 ppm SO_{2i}

buffer used. It was chosen for its excellent buffer capacity at pH 4, as shown in the titration curves in Figure 2-26.

The model was used to find the diffusivities at the experimental conditions: 55°C, pH 3.8, 1000 ppm interfacial sulfur dioxide concentration, total sulfite between 1.9 and 2.6 mM and 0.1 M $CaCl_2$, while the aluminum concentration was varied between 0 and 20 mM. Under these conditions essentially no enhancement was measured, resulting in a buffer diffusivity of 0.02 cm^2/sec. The low apparent diffusivity may result from the formation of large, slow-moving polynuclear aluminum complexes, or it may reflect a slow reaction rate between aluminum complexes and hydrogen ions. In either case, aluminum is a very poor buffer for mass transfer enhancement.

Effects of Buffer Additives on Scrubber Performance

Figure 2-27 has been developed to show the effect of buffer additives on scrubber performance. This graph was developed using the enhancement factor model with adipic acid as the buffer at 55°C in a 0.1 M $CaCl_2$ solution. The ratio of gas to liquid phase mass transfer coefficients (Hk_l°/k_g) was set at 0.2 (Chang, 1979). The figure shows the ratio of the gas phase mass transfer resistance to the overall resistance as a function of buffer added for several different gas and solution compositions.

The ordinate in Figure 2-27 is the ratio of the gas phase mass transfer resistance to the overall mass transfer resistance, which is equal to $(P_{SO_2} - P_{SO_{2,i}})/P_{SO_2}$ if the dissolved sulfur dioxide in the bulk liquid is assumed negligible (Chang, 1979). Thus, unity represents total gas phase resistance. The buffer concentration is represented in a form that is approximately independent of pH on the graph abscissa. Two important scrubber variables are illustrated here: the sulfur dioxide partial pressure and the total sulfite concentration.

The curves illustrate that the buffer is more effective at higher sulfur dioxide partial pressures. As K_g/k_g increases, scrubber performance will improve. This is because with higher sulfur dioxide gas concentrations the system is controlled primarily by liquid-phase resistance in the absence of a buffer, and the buffer reduces liquid-phase resistance.

The curves with zero total sulfite are used to illustrate effects of

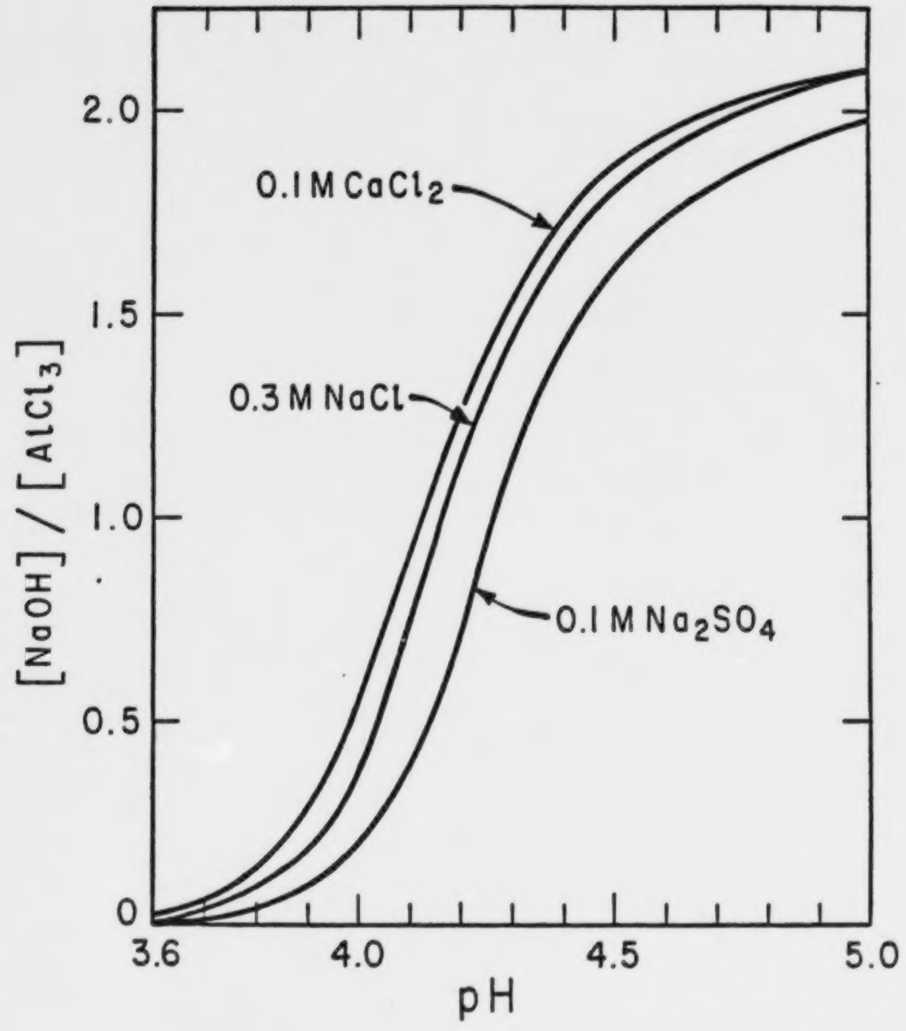


Figure 2-26. Titration of 20 mM Aluminum Chloride

with Sodium Hydroxide in 0.3 M Ionic Strength Solutions at 24°C

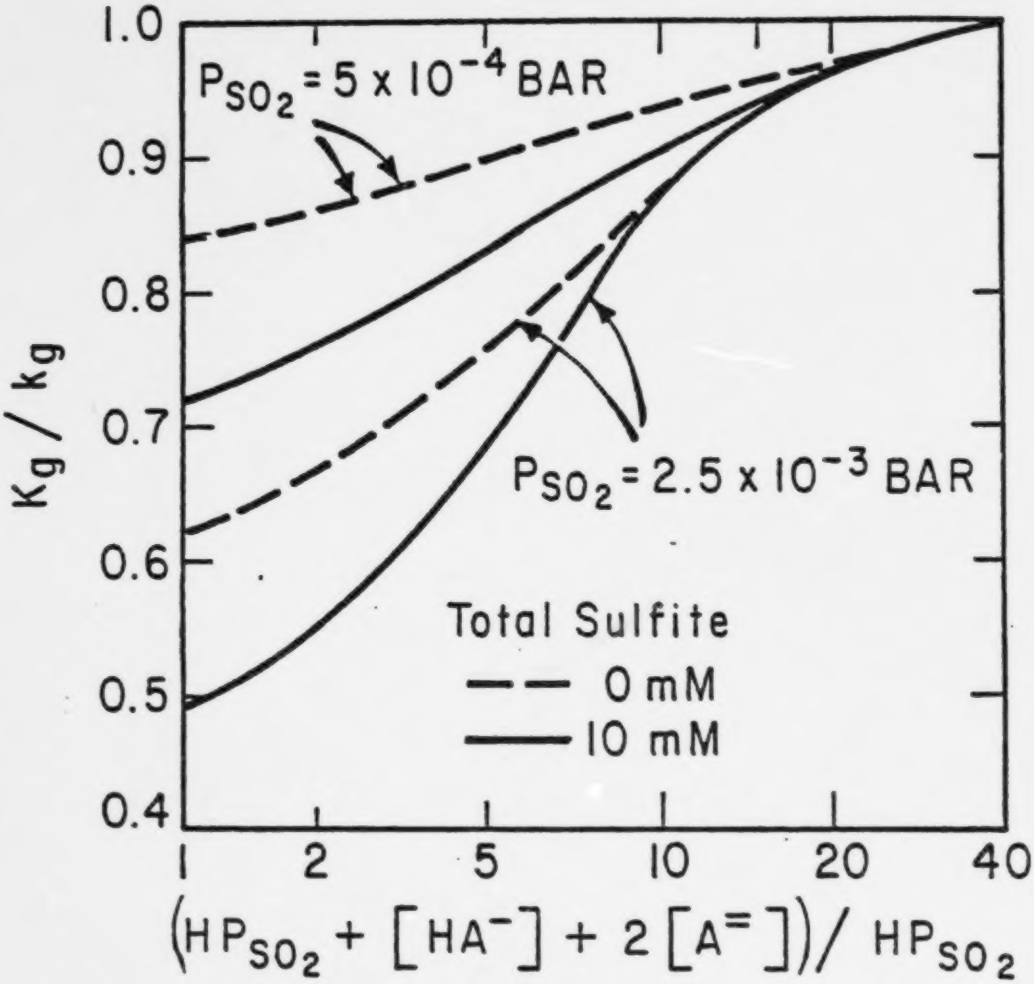


Figure 2-27. Effects of Buffer Addition on Overall

Mass Transfer at 55°C, pH 5.0 in $CaCl_2$ with $Hk_lA/k_gA = 0.2$

forced oxidation. These curves illustrate the beneficial effect of low total sulfite on mass transfer enhancement.

All four curves approach total gas phase control with increasing buffer concentration. Bechtel Corp. (1979) determined that in a typical slurry scrubbing system a 10 to 20 mM buffer concentration should provide most of the benefit from buffer addition. From Figure 2-27, a 10 mM adipic acid concentration with a bulk sulfur dioxide concentration of 2500 ppm, at pH 5 and 10 mM total sulfite results in a K_g/k_g of 0.91. This means that the overall mass transfer coefficient is increased a factor of 1.8. At 500 ppm sulfur dioxide the improvement in overall mass transfer capability is only 20%.

Buffer Additive Economics

The enhancement factor model was used to develop the relative economic costs for eleven buffers considered to be potentially applicable as industrial scrubbing additives. The diffusivities and pK_a values used in the analysis were presented in Tables 2-2 and 2-3.

Tables 2-5 and 2-6 were developed using the enhancement factor model to determine the concentration of a buffer needed to get an enhancement factor of 20. This information was then combined with price information found in the Chemical Marketing Reporter (Oct. 1, 1980) to give the relative cost with respect to adipic acid. Makeup cost is assumed to be proportional to the product of the buffer price and its makeup concentration.

The conditions in Table 2-5 are consistent with a simple slurry system without forced oxidation: pH 5, 1000 ppm SO_2, and 10 mM total sulfite in a 0.1 M $CaCl_2$ solution. Table 2-6 considers the same conditions with a 0 mM total sulfite concentration to simulate the effect of forced oxidation. Factors such as volatility, degradation, and costs involved in making buffers not commercially available were not taken into account in this study.

In the system without forced oxidation (Table 2-5) formic and acetic acids are apparently the two most economical additives. However, the study does not include the losses from volatility which, in this case, could be significant. Also, the environmental impact of these volatile buffers must be investigated. Sulfosuccinic and hydroxypropionic acids, the next least expensive, have good volatility and solubility characteristics, but neither

Table 2-5: Buffer Economics Without Forced Oxidation

Buffer	Buffer Conc (mM)	Price ($/lbmol)	Relative Cost
Formic	17.4	12.28	0.29
Acetic	12.3	21.62	0.36
Adipic	9.5	77.45	1.00
Sulfosuccinic	12.2	43.15	0.72
Sulfopropionic	20.6	34.59	0.95
Hydroxypropionic	14.3	34.59	0.66
Phthalic	14.6	55.58	1.10
Succinic	8.4	134.11	1.53
Benzoic	14.2	57.46	1.11
Glycolic	22.3	39.66	1.20
Lactic	23.8	78.82	2.55

Table 2-6: Buffer Economics With Forced Oxidation

Buffer	Buffer Conc (mM)	Price ($/lbmol)	Relative Cost
Formic	16.3	12.28	0.25
Acetic	13.5	21.62	0.37
Adipic	13.5	21.62	1.0
Sulfosuccinic	12.5	43.15	0.68
Sulfopropionic	22.0	34.59	0.95
Hydroxypropionic	15.5	34.59	0.66
Phthalic	14.8	55.58	1.03
Succinic	9.1	134.11	1.53
Benzoic	14.5	57.46	1.04
Glycolic	20.6	39.66	1.02
Lactic	21.6	78.82	2.13

acid is commercially available, so additional costs will be incurred in developing methods to produce these buffers. The next group contains phthalic, benzoic, sulfopropionic, adipic, and glycolic acids. Of these, phthalic and benzoic have aromatic structures which could result in environmental problems with respect to disposal, and sulfopropionic acid is not commercially available. But adipic and glycolic acids look favorable. The last two buffers, succinic and lactic acids, are not economically attractive.

The forced oxidation case, Table 2-6, results in relative costs that are approximately the same as those observed in forced oxidation, with the exception of glycolic acid. Glycolic acid is significantly more favorable in the forced oxidation case due to its low pK_a value. With forced oxidation the interfacial pH is lower than without forced oxidation, thus the useable buffer capacity of glycolic acid is increased, resulting in a more favorable relative cost.

These results indicate that forced oxidation does not have a significant impact on the relative economics of the buffers. However, in some cases, forced oxidation requires less buffer to achieve an equivalent enhancement, the result of a lower total sulfite concentration and a lower pH operating range.

CONCLUSIONS

1. The surface renewal model of mass transfer with equilibrium reactions was confirmed by experiments at 55°C.
2. The predominant presence of calcium or magnesium in the scrubbing solution reduces the diffusivity of monovalent and bivalent anions by 25 and 45%, respectively, thus reducing the mass transfer rate.
3. A large concentration of dissolved sulfate acts like a buffer, thereby increasing the absorption rate.
4. There is essentially no difference between sodium and magnesium alkali additives for mass transfer enhancement at identical pH values and total sulfite concentrations.
5. The most attractive buffers are:
    a) Adipic Acid
    b) Glycolic Acid

c) Sulfosuccinic Acid

d) Hydroxypropionic Acid

6. Formic and acetic acids would be economically attractive if their volatility could be controlled.

7. The sulfopropionic diffusivity was much lower than estimated, making it less attractive than expected.

8. Aluminum chloride does not significantly increase the rate of mass transfer.

RECOMMENDATIONS

1. The gas-liquid mass transfer model should be incorporated with a liquid-solid mass transfer model to simulate actual scrubber performance.

2. Further investigations in mass transfer enhancement should be directed at phthalic, glycolic, and formic acids and the CO_2/HCO_3^- buffer.

3. The degradation of the recommended buffer additives should be quantified and incorporated into the economic analysis.

4. The volatility of acetic and formic acids should be investigated to determine environmental and economic impacts.

APPENDIX 2-A
NOMENCLATURE

a - thermodynamic activity

A^- - dissociated acid

aq - aqueous phase

C - concentration in the liquid phase, gmol/liter

c_{3j}, c_{4j} - constants related to the activity of the j^{th} ion, Eq. 2-22

cm - centimeter

cm^2 - square centimeter

D - diffusivity, cm^2/sec

D_{eff} - effective diffusivity of a component, cm^2/sec

Fa - Faraday's Number, 23,062 cal/volt equiv

G - gas flow rate, ml/min

g - gas phase

gm - gram

H - Henry's Law Constant, gmol/liter atm

HA - undissociated acid

hp - horsepower

I - ionic strength, gmol/liter

ID - internal diameter

K - thermodynamic equilibrium constant

K_g - overall mass transfer coefficient, gmol/sec

K_a - effective equilibrium constant in concentration units

$k_g A$ - gas phase mass transfer coefficient, gmol/sec atm

$k_l A$ - liquid phase mass transfer coefficient, liter/sec

$k_l^{\circ} A$ - liquid phase physical mass transfer coefficient, liter/sec

L - liquid flow rate, ml/min

M - molar, gmol/liter

mM - millimolar, gmol/liter$\times 10^3$

N_{SO_2} - sulfur dioxide absorption rate, gmol/sec

n_j - charge on the j^{th} ion

P - pressure in the gas phase, bar

ppm - parts per million by volume

P_{SO_2} - sulfur dioxide partial pressure in the gas phase, bar

pH_a - apparent pH value

pK_a - apparent pK value, $K_a = a_{H^+}[A^-]/[HA]$

R - universal gas constant, 0.08205 liter-atm/gmol-K

rpm - revolutions per minute

s - solid phase

sec - seconds

T - absolute temperature, K

t - time

V - molecular volume, cm^3

x - distance in the x direction

α - proportional to

γ_j - activity coefficient of the j^{th} ion

ϕ - enhancement factor

λ - equivalent ionic conductivity

[ ] - concentration

SUPERSCRIPTS

° - ion pair, degrees

SUBSCRIPTS

i - interface

j - component j

w - pure water phase

± - either positive or negative ion

o - bulk

APPENDIX 2-B

COMPUTER MODEL

The computer program presented here was developed by Chang (1979) and used to calculate the enhancement factors in this work. The model is based on the bulk and interfacial equilibrium relationships developed in Chapter 2 which are combined with the species diffusivities to develop the enhancement factor.

```
C     **************************************************
C     FOR SO2:ADIPIC ACID SYSTEM
C     **************************************************
C     A=H2SO3   ,B=H,  C=HSO3   , D=A,  E=HA,  F=H2A,  G=SO3
C     A=B+C
C     C=B+G
C     E=B+D
C     F=H+I
C     AK=BC/A   ,BK=BG/C   ,CK=BD/E,   DK=BE/F
C     **************************************************
C     DATA
C     **************************************************
C     DIFFUSIVITIES
C     **************************************************
        DA=SQRT(1.75E-5)
        DB=SQRT(9.31E-5)
        DC=SQRT(1.33E-5)
        DD=SQRT(0.66E-5)
        DE=SQRT(0.700E-5)
        DF=SQRT(0.731E-5)
        DG=SQRT(0.98E-5)
C     **************************************************
C     IONIC STRENGTH
C     **************************************************
        ZI=0.3
C     **************************************************
C     TOTAL ADIPIC ACID
C     **************************************************
        PH=5.5
        THA=0.0
C     **************************************************
C     ACTIVITY COEFFICIENTS
C     **************************************************
        ZII=ZI**0.5
        ACA=EXP(2.303*(0.075*ZI))
        ACB=EXP(2.303*(0.544)*(-ZII/(1.+0.336*6.0
       0*ZII)+0.4*ZI))
        ACC=EXP(2.303*0,544*(-ZII/(1.0+0.336*4.5*ZII)))
        ACD=EXP(2.303*0.512*(-ZII/(1.0+0.312*3.0*ZII)+0.3*ZI)*4.0)
        ACE=EXP(2.303*0.512*(-ZII/(1.0+0.312*3.0*ZII)+0.3*ZI))
        ACF=EXP(2.303*(0.075*ZI))
        ACG=EXP(2,303*0.512*4.0*(-ZII/(1.0+0.312*4.5*ZII)))
        AI=0.2E-3
C     **************************************************
C     EFFECTIVE EQUILIBRIUM CONSTANTS
C     **************************************************
        AK=9.065E-3*ACA/ACB/ACC
        BK=2,028E-5
        CK=10.0**4.44
        DK=10.0**3.33
        CK=1.0/CK
        DK=1.0/DK
```

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```
C*******************************************************
C     DESIRED BULK GAS CONCENTRATION
C*******************************************************
        DAII=1.0E-3
C*******************************************************
C     TOTAL SULFITES
C*******************************************************
        TS0=3.0E-3
C*******************************************************
C     BULK CONCENTRATIONS
C*******************************************************
5       B0=1.0/(10.0**PH)/ACB
        C0=TS0/(B0/AK+1.0+BK/B0)
        G0=C0*BK/B0
        A0=B0*C0/AK
        D0=C0*BK/B0
        E0=THA/(CK/B0+1.0+B0/DK)
        F0=B0*E0/DK
        D0=CK*E0/B0
        PRINT 3,A0,B0,C0,D0,E0,F0,G0
3       FORMAT(1H ,15X,7(E12.4,3X))
        I=1
        AI=0.2E-3
C     *******************************************************
C     INTERFACE CONCENTRATIONS
C     *******************************************************
        IF((AI-A0).GT.0.0)GO TO 13
        AI=A0*3.0
13      BI=0.5*AI
        J=1
100     EI=(DF*F0+DE*E0+DD*D0)/(DF*BI/DK+DE+DD*CK/BI)
        DI=EI*CK/BI
        FI=BI*EI/DK
        EI=BI*DI/CK
        CI=AI*AK/BI
        GI=CI*BK/BI
        FX=DB*(BI-B0)-DC*(CI-C0)-2.*DG*(GI-G0)
       C+DF*(FI-F0)-DD*(DI-D0)
        IF(FX.GT.0.) GO TO 6
        BI=BI+0.01*AI
        GO TO 100
```

```
C     **************************************************
C     MASS TRANSFER ENHANCEMENT FACTOR
C     **************************************************
  5   CONTINUE
      EN=1.+(DB*(BI-BO)-DG*(GI-GO)-DD*(DI-DO)
     C+DF*(FI-FO))/DA/(AI-AO)
      AII=AI*2.0
      IF(EN.GT.1.0E+5)GO TO 22
      IF(ABS(AII-DAII)/AII.LT.0.01)GO TO 22
      AI=DAII*(AI-AO)/AII+AO
      I=I+1
      IF (I.GT.20) GO TO 20
      GO TO 13
22    GK=1.0/(1.0/(EN*0.2)+1.0)
      RR=(2.0*DO+EO)/AI
20    RRR=(2.0*DO+EO)/AII*2.0
      RRRP=TSO/AII
      ANUM=DK*(1.0+2.0*CK/BO)
      DENO=BO*(1.0+DK/BO+CK*DK/BO**2)
      HA2A=THA*ANUM/DENO
  15  PRINT 4,GK,RR,AI,RRR,AII,HA2A
  4   FORMAT (1H ,6(E15.7))
      PRINT 2,FX,AI,BI,CI,DI,EI,FI,GI,EN
2     FORMAT(1H ,9(E12.4,3X)//)
      IF (EN.GT.1.0E+5) TSO=1.1E-1
      THA=THA+1.0E-3
      IF (THA.LE.20.0E-3) GO TO 5
      STOP
      END
```

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APPENDIX 2-C

EXPERIMENTAL DATA

The data presented here were collected with the experimental apparatus presented in Chapter 2-3. This appendix contains the raw data collected as well as the experimental enhancement factors developed from the raw data.

RUN NO.	LIQUID RATE (ml/min)	GAS RATE (ml/min)	IMPELLER SPEED (rpm)	BULK SO_2 (ppm)	k_1Ax10^3 1/sec
0.3 M SODIUM HYDROXIDE					
401	120	850	380	3010	
402	120	850	450	2825	
403	120	850	560	2350	
701	120	950	415	3165	
702	120	950	470	2925	
703	120	950	540	2680	
704	120	850	415	2825	
705	120	850	415	2815	
706	120	450	415	1665	
707	120	780	370	2825	
0.3 M HYDROCHLORIC ACID					
301	170	150	380	2785	1.4
302	170	150	560	2065	1.5
501	200	180	540	3120	1.9
502	200	100	540	2400	1.3
503	200	80	520	1775	1.5
504	200	150	360	3205	1.4
505	200	150	420	3225	1.5
506	200	150	460	3180	1.5
507	200	150	500	2975	1.6
PURE WATER					
601	175	175	430	1560	6.1
602	175	175	490	1380	7.2
603	170	175	340	1650	5.7
604 605	165	190	520	1645	7.1
	160	250	520	2525	3.6
606	165	300	560	3050	4.0
607	165	225	560	1860	3.0
608	170	110	560	620	

RUN NO.	LIQUID RATE (ml/min)	GAS RATE (ml/min)	SULFITE (mM)	BULK SO_2 (ppm)	INTERFACE SO_2 (ppm)	ENHANCEMENT FACTOR
PURE WATER						
801	160	280	1.30	2820		2.6
802	160	350	1.70	3975		2.1
803	160	150	0.70	1150		4.3
804	170	320	1.60	3185		2.5
805	170	240	1.35	2360		2.2
806	170	180	0.80	1400		4.2
807	160	300	1.50	3510		2.0
808	160	240	1.20	2535		2.4
809	160	200	1.10	2205		2.3
810	160	150	0.65	1250		3.8
0.3 M NaCl, pH 8.5						
1101	150	780	3.20	3605	1535	8.9
1102	150	500	1.90	2375	965	9.6
1103	150	400	3.25	1900	745	10.2
1104	150	300	3.20	1435	280	27.3
1201	150	840	6.35	3375	1080	13.7
1202	150	600	5.00	2520	835	13.2
1203	150	550	5.45	1955	430	25.5
1204	150	470	4.60	1375	20	223
1301	150	1550	7.35	3365	1640	6.8
1302	150	1100	6.55	2565	1215	7.2
1303	150	850	7.30	1955	545	8.4
1304	150	650	9.10	1465	570	10.2
1401	150	1600	7.40	3400	1650	6.7
1402	150	1400	15.05	2400	425	57.0
1403	150	1200	11.15	2065	315	56.6
1404	150	850	9.15	1565	265	58.6
0.1 M $MgCl_2$, pH 8.5						
2001	145	790	4.15	3525	2020	4.8
2002	145	580	2.51	2500	1310	5.9
2003	145	500	1.85	2050	990	6.9

RUN NO.	LIQUID RATE (ml/min)	GAS RATE (ml/min)	SULFITE (mM)	BULK SO_2 (ppm)	INTERFACE SO_2 (ppm)	ENHANCEMENT FACTOR
2011	145	830	3.70	3520	1960	5.2
2012	145	600	2.25	2550	1345	5.9
2013	145	500	2.10	2045	1005	6.8
2014	145	440	2.10	1575	639	9.6
2021	145	760	3.70	3515	1950	5.3
2022	145	575	3.00	2560	1300	6.4
2023	145	500	2.30	2025	895	8.2
2024	145	400	2.10	1500	565	10.9
2031	145	840	5.45	3545	1820	6.2
2032	145	650	4.15	2570	1150	8.1
2033	145	510	3.20	2075	920	8.2
2034	145	410	2.75	1575	620	10.1
0.1 M $MgCl_2$, pH 1.80						
2101	150	325	1.60	1975	1235	4.1
0.2 M $MgCl_2$, pH 1.80						
2102	145	310	1.45	1970	1266	3.8
0.3 M $MgCl_2$, pH1.80						
2103	145	300	1.30	1990	1310	3.5
0.05 M $MgCl_2$, pH 1.80						
2104	145	2 75	1.40	1900	1256	3.8
0.075 M $MgCl_2$, pH 1.80						
2105	145	2 65	1.50	1925	1258	4.1
0.125 M $MgCl_2$, pH 1.80						
2106	145	290	1.60	1925	1247	4.3
PURE WATER, pH 1.80						
2110	145	280	1.20	1850	1270	3.4

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RUN NO.	LIQUID RATE (ml/min)	GAS RATE (ml/min)	SULFITE (mM)	BULK SO_2 (ppm)	INTERFACE SO_2 (ppm)	ENHANCEMENT FACTOR
0.1 M NaCl, pH 1.80						
2111	145	280	1.40	1925	1285	3.9
0.3 M NaCl, pH 1.80						
2112	145	290	1.35	1900	1240	4.1
0.2 M NaCl, pH 1.80						
2113	150	275	1.25	1950	1260	4.0
0.1 M $MgCl_2$, pH 8.5						
2041	150	815	4.50	3475	1793	6.3
2042	145	700	4.80	2650	1125	8.9
2043	145	675	5.30	2350	852	11.6
2044	145	700	8.85	2025	440	24.3
2051	145	1350	13.40	4410	1800	9.5
2052	145	890	11.80	3060	1170	10.6
2053	145	1000	8.25	3825	1810	7.3
2054	145	815	7.30	2910	1169	9.9
2063	145	700	7.45	2410	860	11.8
2064	145	615	7.25	1875	470	19.7
0.1 M Na_2SO_4, pH 4.5						
2201	145	625	3.65	2915	1575	5.6
0.2 M Na_2SO_4, pH 4.5						
2202	145	700	3.40	3060	1575	6.2
0.4 M Na_2SO_4, pH 4.5						
2203	145	735	4.65	3170	1620	6.4
0.8 M Na_2SO_4, pH 4.5						
2204	145	815	4.30	3255	1550	7.0

RUN NO.	LIQUID RATE (ml/min)	GAS RATE (ml/min)	SULFITE (mM)	BULK SO_2 (ppm)	INTERFACE SO_2 (ppm)	ENHANCEMENT FACTOR
0.1 M $MgSO_4$, pH 4.5 2301	145	600	3.20	2855	1565	5.4
0.2 M $MgSO_4$, pH 4.5 2302	145	635	3.10	2925	1588	5.6
0.4 M $MgSO_4$, pH 4.5 2303	145	675	3.80	3015	1580	6.0
0.8 M $MgSO_4$, pH 4.5 2304	145	700	4.25	3035	1550	6.3
0.05 M $NaSO_4$, pH 4.5 2211	145	650	3.05	2650	1230	7.4
0.1 M $NaSO_4$, pH 4.5 2212	145	700	3.35	2800	1290	7.7
0.2 M $NaSO_4$, pH 4.5 2213	145	750	4.00	2850	1230	8.6
0.4 M Na_2SO_4, pH 4.5 2214	145	825	4.30	3000	1240	9.3
0.05 M $MgSO_4$, pH 4.5 2311	145	600	2.65	2600	1289	6.7
0.1 M $MgSO_4$, pH 4.5 2312	145	625	2.55	2700	1345	7.2
0.2 M $MgSO_4$, pH 4.5 2313	145	650	3.35	2665	1251	7.4
0.4 M $MgSO_4$, pH 4.5 2314	145	675	3.65	2765	1305	7.9

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RUN NO.	LIQUID RATE (ml/min)	GAS RATE (ml/min)	SULFITE (mM)	BULK SO_2 (ppm)	INTERFACE SO_2 (ppm)	ENHANCEMENT FACTOR
0.1 M Na_2SO_4, pH 8.5						
2221	145	850	3.70	3050	1245	9.5
2222	145	1000	6.50	3300	1210	11.3
2223	145	1150	9.00	3600	1250	12.4
2231	145	775	6.35	2305	610	18.6
2232	145	825	7.65	2425	600	19.8
2233	145	935	11.20	2625	585	22.9
2234	145	750	3.80	2255	580	16.4
2235	145	800	4.15	2380	610	16.8
2236	145	900	5.35	2570	600	19.2
0.1 M $MgCl_2$, pH 8.5						
2071	145	650	4.90	2000	595	15.9
2072	145	700	6.50	2150	645	15.6
2073	145	750	7.50	2275	645	16.8
0.1 M Na_2SO_4, pH 8.5						
2401	145	675	4.00	2530	725	15.3
2402	145	700	5.30	2615	755	16.3
2403	145	725	5.80	2665	740	17.0
2404	145	760	6.85	2710	700	18.9
2405	145	900	11.15	3085	690	23.9
2406	145	950	11.35	3200	685	24.1
0.1 M $MgSO_4$, pH 8.5						
2501	145	675	4.20	2725	890	11.7
2502	145	770	8.65	3000	925	14.6
2503	145	785	9.90	2945	865	16.0
2504	145	690	6.75	2775	905	13.5
2505	145	725	8.30	2855	900	14.3
2506	145	775	11.3	2950	870	16.9

RUN NO.	LIQUID RATE (ml/min)	GAS RATE (ml/min)	SULFITE (mM)	BULK SO_2 (ppm)	INTERFACE SO_2 (ppm)	ENHANCEMENT FACTOR
0.3 M NaCl, pH 4.5						
2601	145	440	3.05	2250	1025	7.9
2602	145	350	4.25	2000	1015	6.4
2603	145	325	5.35	1930	1010	6.0
2611	145	285	8.70	1800	990	5.4
2612	145	250	13.90	1720	1010	4.7
2613	145	225	19.25	1665	1010	4.2
2614	145	340	5.40	1995	1040	6.1
2615	145	275	10.95	1785	1000	5.1
2616	145	250	13.35	1760	1050	4.7
0.1 M $CaCl_2$, pH 4.5						
2701	145	450	3.60	2250	1000	7.8
2702	145	425	5.50	2210	1025	7.6
2703	145	275	15.55	1790	1010	4.7
2711	145	400	3.90	2120	1000	7.8
2712	145	365	4.30	2030	1005	6.9
2713	145	325	5.75	1935	1020	6.0
2714	145	275	9.80	1770	990	5.2
2715	145	250	11.00	1700	985	4.8
2716	145	250	14.70	1760	1050	4.5
2717	145	275	12.60	1780	1000	5.2
2718	145	240	17.80	1700	1015	4.5
2719	145	200	23.80	1550	975	3.9
0.1 M $MgCl_2$, pH 4.5						
2801	145	435	2.70	2225	1015	7.9
2802	145	375	4.60	2100	1050	6.6
2803	145	350	8.30	2005	1020	6.4
2804	145	290	9.20	1830	1010	5.4
2805	145	275	10.40	1795	1015	5.1
2806	145	250	16.25	1745	1035	4.6

RUN NO.	GAS FLOW (ml/min)	SULFITE (mM)	BUFFER (mM)	BULK SO_2 (ppm)	INTERFACE SO_2 (ppm)	ENHANCEMENT FACTOR
ADIPIC ACID in 0.1 M $CaCl_2$, pH 5.5						
2901	475	2.05	0.0	2350	1035	8.3
2902	725	3.35	5.0	2950	1005	12.7
2903	800	3.15	7.0	3115	990	14.2
2904	1175	4.75	10.0	4020	1040	18.8
ADIPIC ACID in 0.1 M $CaCl_2$, pH 4.2						
3001	400	1.30	0.0	2090	970	7.4
3002	500	2.15	5.0	2385	1005	9.1
3003	625	2.55	10.0	2730	1035	11.7
3004	650	2.55	15.0	2765	1005	11.5
3005	860	2.80	20.0	3140	970	14.4
3006	750	3.10	25.0	3000	995	13.3
3007	800	3.10	30.0	3115	990	14.1
3008	850	3.30	35.0	3255	1010	14.6
3009	1225	4.55	40.0	4110	1020	19.9
3010	650	2.50	10.0	2710	1030	11.3
3011	980	3.05	25.0	3570	1005	16.7
3012	1050	3.15	30.0	3750	1030	17.3
3013	1175	2.30	35.0	3950	970	20.3
ADIPIC ACID in 0.3 M NaCl, pH 4.2						
3101	410	1.80	0.0	2165	1020	7.5
3102	575	2.40	10.0	2605	1035	10.2
3103	650	2.95	20.0	2765	1005	11.9
3104	750	3.35	30.0	3035	1030	13.2
3105	700	3.00	10.0	2860	975	13.1
3106	1075	4.95	40.0	3790	1030	17.6
ACETIC ACID in $CaCl_2$, pH 5.5						
3501	575	3.75	5.3	2780	950	12.6
3502	725	4.75	7.3	2920	970	13.2
3503	1000	5.85	10.7	3600	1005	16.9
3504	1400	5.95	16.0	4490	1035	22.0

RUN NO.	GAS FLOW (ml/min)	SULFITE (mM)	BUFFER (mM)	BULK SO_2 (ppm)	INTERFACE SO_2 (ppm)	ENHANCEMENT FACTOR
ACETIC ACID in 0.3 M NaCl, pH 5.5						
3601	700	3.65	5.3	2890	1005	12.3
3602	800	4.55	8.8	3170	1050	13.3
3603	875	5.55	11.0	3270	960	15.8
3604	1125	6.90	15.0	3850	975	19.4
SULFOPROPIONIC ACID in 0.1 M $CaCl_2$, pH 5.5						
3701	635	3.95	3.7	2565	1000	10.3
3702	710	4.35	7.4	2800	1070	10.8
3703	785	3.95	10.0	2870	970	12.9
3704	925	5.00	15.4	3250	1055	13.6
SULFOPROPIONIC ACID in 0.3 M NaCl, pH 5.5						
3801	550	2.85	3.3	2385	1015	8.9
3802	625	3.70	6.7	2555	1005	10.1
3803	850	5.50	10.0	3040	1000	13.4
3804	1100	5.40	15.3	3560	1000	16.9
SULFOSUCCINIC ACID in 0.1 M $CaCl_2$, pH 5.5						
4101	775	5.20	4.6	2860	985	12.6
4102	1015	6.40	9.0	3390	980	16.0
4103	700	3.70	2.5	2705	990	11.4
4104	950	5.90	7.5	3270	1020	14.5
4105	1200	6.40	10.0	3835	1085	16.6
SULFOSUCCINIC ACID in 0.3 M NaCl, pH 5.5						
4201	725	3.50	2.5	2825	1065	10.9
4202	850	4.30	5.4	3100	1065	12.5

RUN NO.	GAS FLOW (ml/min)	SULFITE (mM)	BUFFER (mM)	BULK SO_2 (ppm)	INTERFACE SO_2 (ppm)	ENHANCEMENT FACTOR
HYDROXYPROPIONIC ACID in 0.1 M $CaCl_2$, pH 5.5						
4301	700	5.05	5.1	2700	985	10.1
4302	800	4.20	8.0	2890	955	13.4
4303	1050	4.65	13.5	3550	985	16.9
4304	600	4.70	2.2	2465	975	8.9
4305	750	5.35	6.8	2860	1040	11.5
ALUMINUM CHLORIDE in 0.1 M $CaCl_2$, pH 3.5						
4401	575	2.60	5.0	2425	995	6.7
4402	600	2.50	10.0	2490	1005	7.0
4403	600	2.50	15.0	2500	1015	7.0
4404	600	2.50	20.0	2500	1015	7.0
4405	550	1.90	0.0	2390	1020	6.4

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SECTION 3

DEGRADATION OF ADIPIC ACID CONJUGATED WITH SULFITE OXIDATION

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SECTION 3

ABSTRACT

Buffer additives have been proposed to enhance SO_2 removal and $CaCO_3$ utilization in slurry scrubbing for flue gas desulfurization. Adipic acid is the most promising buffer, but it degrades in the presence of sulfite oxidation. This work investigated oxidative degradation of adipic acid and other dicarboxylic acids as a function of pH and concentrations of carboxylic acid, manganese, and thiosulfate. Experiments were carried out in a batch reactor oxidizing 1 M $CaSO_3$ slurry containing 2-20 mM organic acid at 55°C and pH 4.0-5.5. The rate of sulfite oxidation was generally controlled by O_2 mass transfer with dissolved Mn or low pH, but was less at pH 5.0 or 5.5 without Mn. Sulfite oxidation was inhibited by thiosulfate and hydroxycarboxylic acids. Sulfite oxidation was a necessary and sufficient condition for degradation. The rate of degradation was proportional to the adipic acid concentration and to the rate of sulfite oxidation. Degradation was inhibited by 0.3-1.0 mM Mn and unaffected by dissolved Fe. The degradation rate of adipic acid was 0.015 moles per mole sulfite oxidized with 10 mM adipic acid at pH 5.5. The rate was reduced by a factor of 2 at pH 4.3 without Mn and at pH 5.5 with Mn. At pH 4.3 with Mn, it was reduced by a factor of 15. Glutaric acid was the major retained degradation product in the presence of Mn, while 4-carboxybutanol with the major product in the absence of Mn.

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CHAPTER 3-1

INTRODUCTION

Lime/limestone slurry scrubbing is currently the dominant technology for stack gas desulfurization (Figure 3-1). Flue gas containing 500-5000 ppm SO_2 is contacted with a slurry of product solids at the gas adiabatic saturation temperature, typically 50-55°C. Recycle slurry is given reaction time in the crystallizer to dissolve CaO or $CaCO_3$ and precipitate $CaSO_3$. $CaSO_4$ is also produced to a limited extent because of O_2 in the flue gas. $CaSO_3/CaSO_4$ waste solids are separated and disposed of. Solution is retained in the system. One common modification of this process sparges air into the crystallizer to achieve forced oxidation of $CaSO_3$ to $CaSO_4$. $CaSO_4$ solids (gypsum) are easier to dewater and dispose of than $CaSO_3$ solids (Rossoff, 1974).

Buffer additives have been proposed to enhance SO_2 absorption with $CaO/CaCO_3$ slurry scrubbing (Rochelle and King, 1978; Chang and Rochelle, 1980; Weems, 1981). Adipic acid is one of the most attractive alternatives. It has been successfully tested by EPA with and without forced oxidation in the 0.1 MW pilot plant at Research Triangle Park and the 10 MW venturi/spray and turbulent contact absorbers (TCA) at the TVA Shawnee Power Plant (Burbank and Wang, 1979; Burbank et al., 1980). EPA has supported demonstration of adipic acid in a full scale $CaCO_3$ TCA system at Springfield, Missouri (Hicks et al., 1980). Typically, 10 to 20 mM of adipic acid will improve SO_2 removal from 75-85% to 95-99%.

Adipic acid ($HOOC-(CH_2)_4-COOH$) is a dicarboxylic organic acid used primarily as a monomore for nylon 66 but also approved as a food additive. It has two pKa values, 4.5 and 5.5 (Sillen and Martell, 1964). However, accumulation of $CaCl_2$ typically depresses the buffering points to about pH 4.0 and 5.0 (Cavanaugh, 1978). Due to its buffering effect, adipic acid is capable of limiting the pH drop at the gas/liquid interface as SO_2 is absorbed into the scrubbing solution. Also, adipic acid in solution as calcium adipate will reduce the need for $CaCO_3$ or $CaSO_3$ dissolution in the scrubber to provide

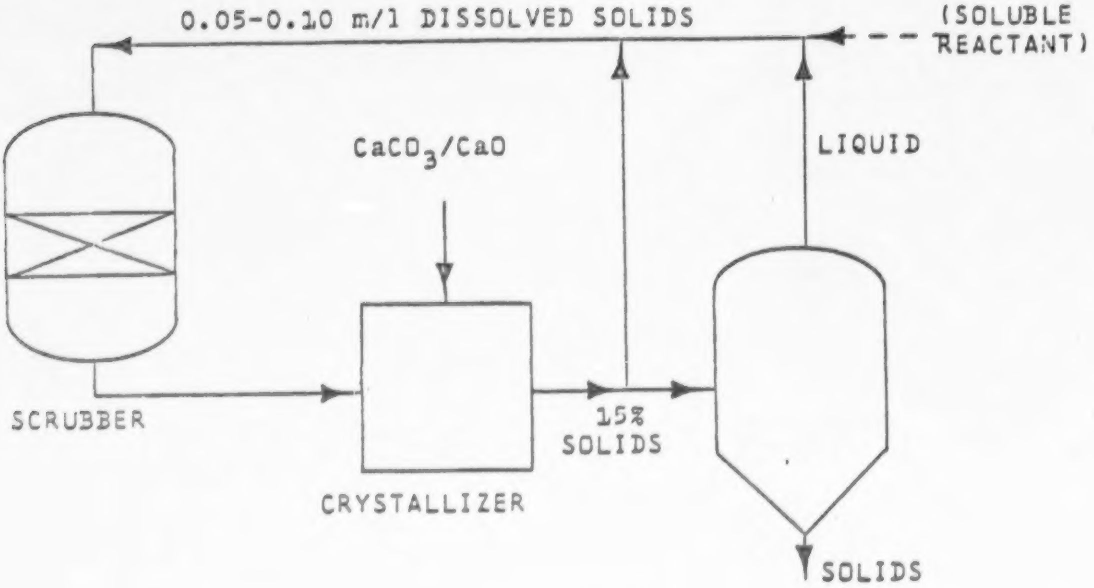

0.05-0.10 m/l DISSOLVED SOLIDS
(SOLUBLE REACTANT)
$CaCO_3$/CaO
LIQUID
SCRUBBER
15% SOLIDS
CRYSTALLIZER
SOLIDS

Figure 3-1. Simple Slurry Scrubbing

the alkalinity for SO_2 absorption. As a result, scaling in the scrubber by $CaSO_3$ or $CaSO_4$ can be minimized.

Testing of adipic acid at the Shawnee and RTP scrubber facilities has shown that the required makeup of adipic acid is greater than the amount of adipic acid lost with solution entrained in the waste solids. The additional losses of adipic probably result from coprecipitation of $CaSO_3$ and adipic acid in the waste solids and from oxidative degradation of adipic acid. Typical adipic acid losses calculated of operation of the RTP scrubber are given in Table 3-1. Apparently, the use of forced oxidation is favored over natural oxidation despite the greater adipic acid loss through degradation. Forced oxidation reduces the adipic acid loss by producing an easily dewatered solid waste and by eliminating coprecipitation with $CaSO_3$.

Laboratory research at Radian has shown that sulfite oxidation is a necessary and sufficient condition for adipic acid degradation to occur (Meserole et al., 1979). The rate of adipic acid degradation is dependent upon the rate of sulfite oxidation. Adipic acid degrades approximately four times faster as a result of forced oxidation. pH also affects the rate of adipic acid degradation. Field testing at Shawnee with high levels of dissolved Mn impurity has shown that degradation of adipic acid is minimized at pH less than 5.0 (Burbank et al., 1980).

The primary objective of this work is to quantify oxidative degradation of adipic acid as a function of pH, adipic acid concentration, manganese concentration, and sulfite oxidation rate. These results should confirm and verify those of field testing.

Table 3-1: Typical Adipic Acid Losses in RTP Pilot Plant, pH 6.1

	Forced Oxidation[a]	Natural Oxidation[b]
% Oxidation	99	15
Filter Cake Solids, %	86	50
Mole Adipic Acid Lost[c] / Mole SO_2 Absorbed		
Solution	0.00014	0.0021
Coprecipitation[d]	0	0.00051
Degradation	0.0019	0.00056
Total Loss	0.002	0.0032

---

[a] Borgwardt, R.H., EPA-IERL Progress Report 38, Dec., 1978

[b] Borgwardt, R.H., EPA-IERL Progress Report 37, Nov., 1978

[c] See Appendix 3-A for calculation

[d] Meserole et al., 1980

CHAPTER 3-2

LITERATURE REVIEW

SUMMARY

Under typical scrubber conditions, 50-60°C and pH 4-6, degradation of adipic acid is conjugated with sulfite oxidation. The major degradation products are valeric and glutaric acids with succinic, propionic and malonic acids in lesser amount. A rate expression proposed for adipic acid degradation has the following form:

$$\frac{d[A]}{dt} = k_d \frac{d[SO_3^=]}{dt} [A]$$

The degradation rate constant k_d should be a function of bisulfite concentration only and is used to correlate degradation results obtained under different operation conditions.

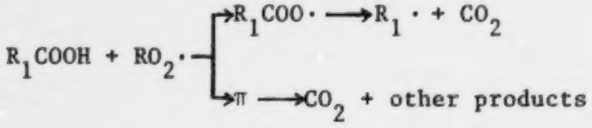
Previous field and laboratory data are consistent with the hypothesis that Mn inhibits degradation at low pH. Much higher rates of degradation were observed in bench-scale testing without Mn at Radian than in prototype testing with Mn at Shawnee.

CONJUGATED OXIDATION

Under typical scrubber conditions, 50-60°C and pH 4-6, the primary mechanism of carboxylic acid degradation is probably conjugated oxidation. In the absence of other oxidizing species, carboxylic acids do not oxidize. However, when alcohol or hydrocarbons are oxidized in the presence of carboxylic acids, the carboxylic acids are also oxidized. Thermal degradation occurs at 270-330°C in aqueous solution or 50-100°C in 1-2 M sulfuric acid solution (Agabekov and Mickevich, 1967; Kiselva and Dudkin, 1967). Photochemical degradation needs light and catalyst (Kraeutler and Bard, 1978; Kuhule et al., 1972). Microbial degradation requires microorganisms that are unlikely to survive at scrubber conditions (Keith, 1978; Grulas, 1976; Hammond and Alexander, 1972).

Degradation of C_2-C_{10} carboxylic acids has been observed in hydrocarbon solutions undergoing oxidation (Tinker, 1970; Denisov, Mitskevich, and Agabekov, 1968; Berezin, Denisov, and Emanuel, 1966). Two observations support the hypothesis that carboxylic acid degradation is conjugated with free radical oxidation of other chemical species. (1) Degradation of carboxylic acids can be inhibited by free radical scavengers such as phenol, oxygen, or β-naphthol (Sheldon and Kochi, 1972; Agabekov and Mickevich, 1967). (2) Degradation does not take place in the absence of hydrocarbon oxidation (Nadin and Mitskevich, 1972; Tinker, 1970).

Two mechanisms have been proposed for carboxylic acid degradation (Denisov, Mitskevich, and Agabekov, 1977):



$$R_1COOH + RO_2\cdot - \left[\begin{array}{ll} \rightarrow R_1COO\cdot \longrightarrow R_1\cdot + CO_2 & \qquad \text{3-1a} \\ \rightarrow \pi \longrightarrow CO_2 + \text{other products} & \qquad \text{3-1b} \end{array} \right.$$

The free radical, $RO_2\cdot$, may attack the carboxylic acid, R_1COOH, to form a carboxylate radical or some other intermediate, π, which then decomposes to give CO_2.

Degradation of monocarboxylic and small dicarboxylic acids usually takes place through the carboxylate radical. The free radical attacks the stronger O-H bond because of its greater reactivity (Berezin and Rigimova, 1962). The rate of degradation is independent of the length of the carboxylic acid molecule and is a function of the rate of oxidation only.

Dicarboxylic acids with more than six carbons degrade predominantly through the intermediate product. The C-H bond of the methylene group is preferentially attacked, possibly because the O-H bond is not accessible due to an intramolecular hydrogen bond formed within the molecule. Attack of the C-H bond results in a rupture of the C-C bond and produces smaller dicarboxylic acids. The rate of degradation usually increases linearly with increase in the number of methylene groups (Agabekov and Mickevich, 1967).

ADIPIC ACID DEGRADATION

Mechanism

The mechanism of oxidative degradation of adipic acid in the liquid phase at 170°C has been verified by Agabekov and Mickevich (1968) using tracer atoms. The carboxyl groups in adipic acid were labeled with ^{14}C, and the CO_2 evolution was monitored. During the initial stage of adipic acid oxidation, appearance of non-radioactive CO_2 along with radioactive CO_2 indicated formation of smaller carboxylic acids or their radical which were also subjected to degradation. A material balance for adipic acid and its degradation products showed that the actual amount of CO_2 formed was much larger than the amount calculated assuming that degradation took place only from the carboxyl groups. Therefore, adipic acid degradation must occur to certain extent through rupture of the C-C bonds.

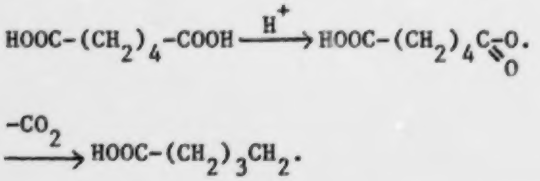
Tinker (1970) studied adipic acid degradation in cyclohexane undergoing air oxidation in the presence of colbaltic ions. Adipic acid degradation only occurred in the presence of cyclohexane oxidation, and in the absence of cyclohexane oxidation, adipic acid was stable. Degradation also occurred in the absence of cobaltic ions, therefore it is not induced by cobaltic ions.

The extent of adipic acid degradation was a function of cyclohexane oxidation. For equal moles of oxygen consumed, cyclohexane oxidation decreased from 30% at 90°C to 15% at 150°C, and percent of adipic acid degradation increased from 4% to 25% at the same time. More oxygen was consumed for reactions other than cyclohexane oxidation at higher temperatures.

Products

Figure 3-1 shows all the possible degradation products of adipic acid, which include monocarboxylic acids, smaller dicarboxylic acids, alkanes, carbon monoxide, and carbon dioxide. Malonic acid ($HOOC{-}CH_2{-}COOH$) and oxalic acid ($HOOC{-}COOH$) are less likely degradation products, because they are unstable under oxidative conditions.

Adipic acid yields valeric acid ($H_3C(CH_2)_3COOH$) according to the following set of reactions (Berezin, Denisov, and Emanuel, 1966):



$$HOOC{-}(CH_2)_4{-}COOH \xrightarrow{H^+} HOOC{-}(CH_2)_4\underset{\displaystyle O}{\overset{\|}{C}}{-}O\cdot$$

$$\xrightarrow{-CO_2} HOOC{-}(CH_2)_3CH_2\cdot \qquad 3\text{-}2$$

The free valeric acid radical can abstract a hydrogen atom from an adjacent

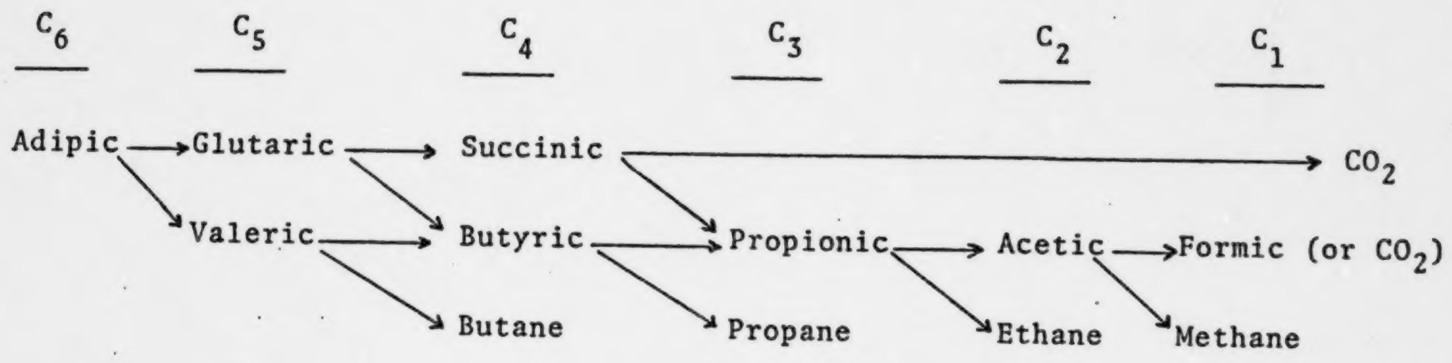

C_6
C_5
C_4
C_3
C_2
C_1
Adipic
Glutaric
Succinic
CO_2
Valeric
Butyric
Propionic
Acetic
Formic (or CO_2)
Butane
Propane
Ethane
Methane

Figure 3-2. Oxidative Degradation of Adipic Acid

molecule and yield valeric acid, or the valeric acid radical can react with oxygen and produce a primary acid peroxide:

$$HOOC\text{-}(CH_2)_3CH_2\cdot \longrightarrow HOOC\text{-}(CH_2)_3\text{-}CH_2OOH \qquad 3\text{-}3$$

The primary acid peroxide is unstable and decomposes in two ways. The first involves dissociating one molecule of water with the formation of glutaric aldehyde, which is then oxidized to glutaric acid. The second route is a homolytic fracture of the O-O bond producing two free radicals:

$$HOOC\text{-}(CH_2)_3\text{-}CH_2\text{-}O\text{-}OH \longrightarrow HOOC\text{-}(CH_2)_3\text{-}CH_2O\cdot + \cdot OH \qquad 3\text{-}4$$

The free hydroxyl reacts with surrounding molecules, forming water and creating a free radical. The alkoxy radical tends to decompose and yield a formaldehyde molecule and a low acid radical:

$$HOOC\text{-}(CH_2)_3CH_2O\cdot \longrightarrow HOOC\text{-}(CH_2)_2CH_2\cdot + CH_2O \qquad 3\text{-}5$$

The butyric acid radical reacts by the same two routes as the valeric acid and yields lower acid products.

SULFITE OXIDATION

Sulfite oxidation undoubtedly proceeds by a free radical mechanism (Backstrom, 1934; Chen and Barron, 1972; Barron and O'Hern, 1966), but there is no generally accepted rate expression (Srivastava et al., 1968; de Wall and Okeson, 1966; Chen and Barron, 1972; Barron and O'Hern, 1966). A typical reaction sequence for cobalt catalyzed oxidation of sulfite is given below:

$$SO_3^{=} + Co^{+3} \xrightarrow{k_1} Co^{+2} + \cdot SO_3^{-} \qquad 3\text{-}6a$$

$$\cdot SO_3^{-} + O_2 \xrightarrow{k_2} \cdot SO_5^{-} \qquad 3\text{-}6b$$

$$\cdot SO_5^{-} + SO_3^{=} \xrightarrow{k_3} SO_5^{=} + \cdot SO_3^{-} \qquad 3\text{-}6c$$

$$SO_5^{=} + SO_3^{=} \xrightarrow{k_4} 2SO_4^{=} \qquad 3\text{-}6d$$

$$\cdot SO_5^{-} + \cdot SO_5^{-} \xrightarrow{k_5} \text{inert products} \qquad 3\text{-}6e$$

In this mechanism the rate of sulfite oxidation given by Reaction 3-6c is proportional to the concentration of sulfite ion and of the free radical, $.SO_5^-$.

Hudson (1980) investigated the effects of initial pH and manganese concentration on the batch oxidation of 0.1 M calcium sulfite slurries without pH control. Typical sulfite oxidation behavior at pH 5.1, 1800 rpm, and 50°C is shown in Figure 3-2. The rate of oxidation was controlled by mass transfer of O_2 from 0-4 minutes, then it became controlled by reaction kinetics after 4 minutes as dissolved sulfite was depleted in the solution. The initial oxidation rate was 1.61 M/hr.

A pH drop of 0.2 to 0.5 units was observed in the initial stages of sulfite oxidation with and without Mn at initial pH 4.5-5.1 and 50°C. At initial pH 4.5, the pH continued to decrease rapidly, and at initial pH 5.1, the pH behavior was irregular.

Figure 3-3 gives the initial rate of oxidation as a function of pH with and without Mn at 50°C. Addition of 1.6 mM Mn increased the oxidation rate 54% at pH 5.1 and 27% at pH 4.5. At higher Mn concentration, 40 mM, the rate of oxidation is controlled by reaction kinetics only.

ADIPIC ACID DEGRADATION RATE EXPRESSION

A rate expression for adipic acid degradation under scrubber conditions was proposed by Rochelle (Meserole et al., 1979):

$$\frac{d[A]}{dt} = k_d \frac{d[SO_3^=]}{dt} [A] \qquad 3\text{-}7$$

The rate is a function of adipic acid concentration and the rate of sulfite oxidation.

This expression is derived based on two assumptions, which can be stated mathematically as:

(1) $$\frac{d[A]}{dt} = k_1[R.][A] \qquad 3\text{-}8$$

(2) $$\frac{d[SO_3^=]}{dt} = k_2[R.][HSO_3^-] \qquad 3\text{-}9$$

Solving for the free radical concentration in Eq. 3-9 and substituting it

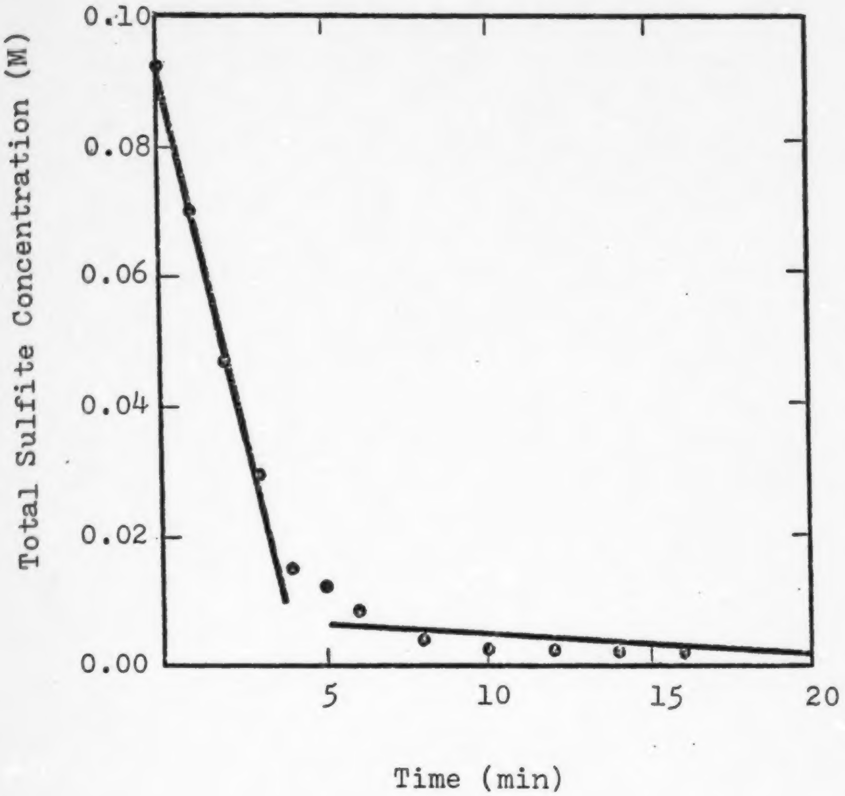


Figure 3-3. Oxidation of $CaSO_3$ Slurry at pH 5, 50°C, 1800 rpm, with no Added Mn

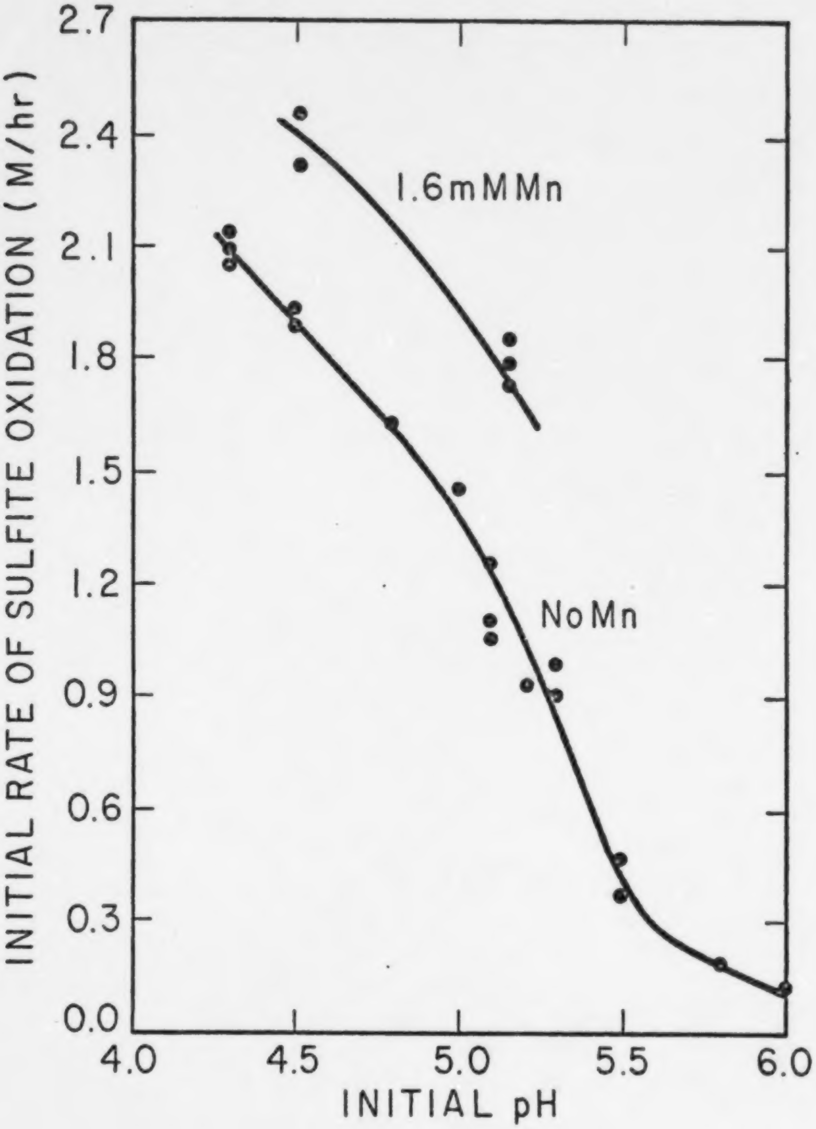


Figure 3-4. Rate of Sulfite Oxidation as a Function of pH

into Eq. 3-8 for [R.] gives:

$$\frac{d[A]}{dt} = \frac{k_1[A]}{k\ [HSO_3^-]} \quad \frac{d[SO_3^=]}{dt} \qquad 3\text{-}10$$

The rate constant k_d in Eq. 3-7 is the lumped rate constant of k_1, k_2, and bisulfite concentration. It is inversely proportional to the bisulfite concentration and is only a function of the variables which affect the bisulfite concentration.

In a batch oxidation experiment, the concentration of adipic acid can be related to total sulfite concentration by eliminating time in Eq. 3-7 and integrating the resulting equation:

$$\ln[A] = k_d[SO_3^=] + C \qquad 3\text{-}11$$

Eq. 3-11 suggests that plotting the natural logarithm of adipic acid concentration versus total sulfite concentration will give a straight line and the slope of the line is the rate constant k_d.

ADIPIC ACID DEGRADATION UNDER SCRUBBER CONDITIONS

Adipic acid was initially tested under scrubber conditions at Research Triangle Park (RTP). Overall material balance for the scrubber system indicated loss of adipic acid (Borgwardt, Nov. 1978), and odor of valeric acid was detected in the scrubber liquor and solids (Borgwardt, Nov. 1977, Sept. 1978, April 1980). Adipic acid degradation and odor of valeric acid were later confirmed at the Shawnee prototype plant (Burbank and Wang, 1979).

Radian was contracted by EPA to identify adipic acid degradation products and determine the necessary conditions for degradation. Radian analyzed the samples collected at RTP and Shawnee and found glutaric and valeric acids to be the major degradation products. Furthermore, conjugated sulfite oxidation was confirmed as a necessary and sufficient condition for adipic acid degradation (Meserole et al., 1979). A similar design of reactor was adapted by the University of Texas to study degradation of adipic acid and other buffers (Garcia, 1980).

Reduced adipic acid degradation has been observed at Shawnee in the presence of Mn at pH below 5.0 (Burbank et al., 1980). Initial work at the

University of Texas also found that degradation could be inhibited in the presence of manganese. These observations have led RTP and Shawnee to study the effects of pH and manganese on adipic acid degradation.

To verify the low degradation at Shawnee and characterize the effects of key operating variables on adipic acid degradation, Radian initiated a series of studies in a bench scale scrubber. Scrubber solids were also analyzed to quantify adipic acid loss through coprecipitation as a function of degree of sulfite oxidation.

Radian Work

During Radian's early laboratory work, a 500 ml, closed glass, batch reactor was used to study degradation (Meserole et al., 1980). Concentration of the calcium sulfite slurry for each run varied between 0.16 and 0.34 M, and initial adipic acid concentration was 13.7 mM. The slurry was magnetically stirred. The temperature was controlled at 50°C in a water bath. Oxygen was supplied through a presaturator at 20 ml/min. The pH was allowed to drift from its initial value. Sulfite oxidation rate in this apparatus was slow, typically 0.008 M/hr at pH 4.5 and 6.0.

Only four runs were made in the batch reactor at pH 4.5 and 6.0. The data are given in Table B-3 of Appendix B. The degradation rate constant k_d decreased from 1.8-2.7 M^{-1} at pH 6.0 to 0.4-0.9 M^{-1} at pH 4.5. More detailed study of adipic acid degradation was carried out in a similar batch reactor in this work and Garcia's work (1980).

Radian's bench scale system consisted of a packed or sparged scrubber with recirculating slurry from the hold tank. Laboratory operation used synthetic flue gas, and field operation used on-site flue gas. Results of the bench scale work are given in Table 3-11 of Appendix 3-B. Laboratory studies did not verify the Shawnee low degradation at pH 4.6 to 4.8 and generally gave k_d of 0.7-1.3 M^{-1}. Reduced degradation at pH 5.1 was observed in one run with 0.2 mM manganese. Degradation was also reduced by increasing the dissolved sulfite concentration at pH 5.5 or lowering the temperature of the slurry from 125°F to 94°F at pH 4.6. Field testing at Shawnee and RTP did not verify the low degradation at pH 4.6 but showed that degradation was inhibited at pH 4.6 with 2.4 mM Mn.

The scrubber solids taken during the bench scale tests were analyzed for coprecipitated adipic acid. Analyses showed that solids over thirty percent oxidized (molar basis) contained no adipic acid. Coprecipitation of adipic acid becomes significant only when the solids are under twenty percent oxidized (Terry et al., 1981).

During the batch reactor study, Ion Chromatography (IC) and Gas Chromatography (GC) were used to quantify adipic acid and its degradation products (Meserole et al., 1980). Valeric and glutaric acids were identified as major degradation products. At pH 6.0, 50°C, and 20 ml/min oxygen flow rate, the amount of glutaric and valeric acids formed was approximately 15% and 25% (molar basis) of the total adipic acid degraded. At higher oxygen flow rate, 40 ml/min, glutaric acid was not found, and the level of valeric acid was about 50% of total adipic acid degraded.

Sample solutions taken during the bench scale tests were analyzed by IC, GC, and Ion Chromatography Exclusion (ICE). A new peak has been detected on IC but not identified. Initial GC analyses have identified additional degradation products, propionic, succinic, and malonic acids. Formation of the degradation products seems to vary as a function of the rate of sulfite oxidation and manganese concentration (Jarvis and Schubert, 1981).

Work at Research Triangle Park (RTP)(Borgwardt, 1977-80)

The scrubber system at RTP consists of a single-loop, 300 cfm spray scrubber and a single hold tank during natural oxidation. Another hold tank was added during forced oxidation. The system was an open system, and soluble tracers, Na^+ and Cl^-, were added to the slurry to indicate the amount of solution loss. Scrubber solids analysis was neglected at RTP, and rate constants were calculated based on adipic acid losses through degradation and coprecipitation. Carboxylic acids were analyzed by IC.

RTP test results from Nov. 1977 to Sept. 1980 are given in Table 3-9 of Appendix 3-B. Most of the runs were conducted under natural oxidation; therefore, the calculated k_d values are probably on the high side because of loss by coprecipitation. k_d was 0.2-0.9 M^{-1} at pH 4.6 to 6.1. No consistent variation with pH was observed. Several runs with ferrous iron and flyash showed no effect on degradation.

Shawnee Work

Tests at the EPA-sponsored Shawnee prototype facility were conducted in a variety of 10 MW scrubber systems with good material balance usually closed within 95% (Burbank et al., 1980; Bechtel, 1980). The slurry solution normally contained 0.1-1.0 mM of manganese accumulated from the flue gas or limestone. Sample solutions were analyzed for adipic acid by the silicic acid titration method, which measures total carboxylic acid concentration. In this method, carboxylic acids were adsorbed on silicic acid solids then desorbed in chloroform. Titration of the chloroform with sodium hydroxide solution determined the total carboxylic acid concentration. Adipic acid concentration thus determined should be somewhat higher than its actual value.

A summary of Shawnee data is given in Table B-2 of Appendix 3-B. Zero degradation was observed in several runs at pH 4.6-4.8. k_d did not vary consistently with pH and was generally lower than the Radian and RTP values. This was perhaps due to the high oxidation at Shawnee which reduced losses through coprecipitation and the higher adipic acid concentration analysis by the silicic acid titration method. At pH 5.0 to 5.2, runs with 0.6-1.1 mM Mn had lower k_d values than runs with Mn concentration below 0.1 mM. Therefore, 0.1 mM Mn is not sufficient to inhibit degradation.

CHAPTER 3-3

EXPERIMENTAL APPARATUS AND PROCEDURE

SUMMARY

Twenty-six experiments were made to study adipic acid degradation during oxidation of calcium sulfite slurries. In runs one through seven, a glass batch reactor was used, and in runs eight through twenty-six, a plexiglass batch reactor with improved pH and agitation control was used.

In a typical experiment, 1.0 M synthesized calcium sulfite solids were slurried and oxidized in solution containing 5 to 20 mM adipic acid. About eight to ten slurry samples were taken during the course of sulfite oxidation and analyzed for total sulfite concentration by iodine titration. The slurry samples were filtered and diluted then analyzed for adipic acid by Ion Chromotography (IC) or Ion Chromotography Exclusion (ICE). Atomic absorption spectrophotometry was used to determine the concentration of manganese and iron in some filtered samples.

SYNTHESIS OF CALCIUM SULFITE SOLIDS

Calcium sulfite solids were either synthesized in the laboratory or purchased from ICN Pharmaceuticals, Inc. The laboratory calcium sulfite solids were prepared by dropwise titration of 1 M Na_2SO_3 into 1 M $CaCl_2$ according to the following reaction:

$$Na_2SO_3(aq) + CaCl_2(aq) \longrightarrow CaSO_3(s) + 2NaCl(aq) \qquad 3\text{-}12$$

The slurry solids were vacuum filtered, reslurried with distilled water, filtered again, washed with acetone, and dried at 60°C. A verification of the sulfite concentration of the solids was later made using iodimetric titration. Purity of the solids thus prepared was usually above 90%. The major impurity in the solids was assumed to be $CaSO_4 \cdot 2H_2O$ formed by oxidation during preparation.

Purity of the purchased solids determined by iodine titration was approximately 65%. Later analyses of reactor solutions suggested that the purchased solids contained at least 5 ppm Mn.

APPARATUS

Glass Reactor

Runs one through seven were made in a closed, glass, batch reactor (Figure 3-5). The reactor was a one-liter, three-necked, round bottom flask. It was wrapped with heating tape controlled by a mercury thermoregulator to give 55°C slurry. Pure oxygen gas was presaturated with water at about 25°C in a fritted glass impinger. The saturated gas was sparged through a gas bubbler into the reactor. Vent gas passed through a condenser and the condensed water was returned to the reactor. This apparatus incorporated an additional gas washing bottle containing 0.05 N NaOH for the collection of CO_2 generated during the decarboxylation reaction. The slurry solution was magnetically stirred during the tests. Normally a clear liquid layer was observed at the surface of the slurry solution, indicating that the slurry solution was not homogeneously mixed.

Plexiglass Reactor

In the glass reactor, agitation by the magnetic stirrer was insufficient and nonreproducible and pH was uncontrolled. In experiments after run A7, these disadvantages were corrected by using a plexiglass reactor with controlled agitation and pH.

The pH-Stat apparatus is shown in Figure 3-6. It consisted of a three-liter plexiglass batch reactor and a Fisher Titrimeter II Titration System. Since the reactor was an open system, no gaseous products could be trapped. This was satisfactory since identification or quantification of the gaseous products was not an objective of this study.

The detail components of the reactor are shown in Figure 3-7. The reactor was 14 cm in diameter and height with an o-ring sealed lid. It was baffled on four sides to eliminate vortex formation during solution agitation. A nozzle on the size of the reactor served as a sample port. A three-bladed, 2.5 cm marine propeller was driven on the fast shaft of a variable speed motor. Agitator speed was measured by counting rotations of a slow shaft directly linked to the agitator.

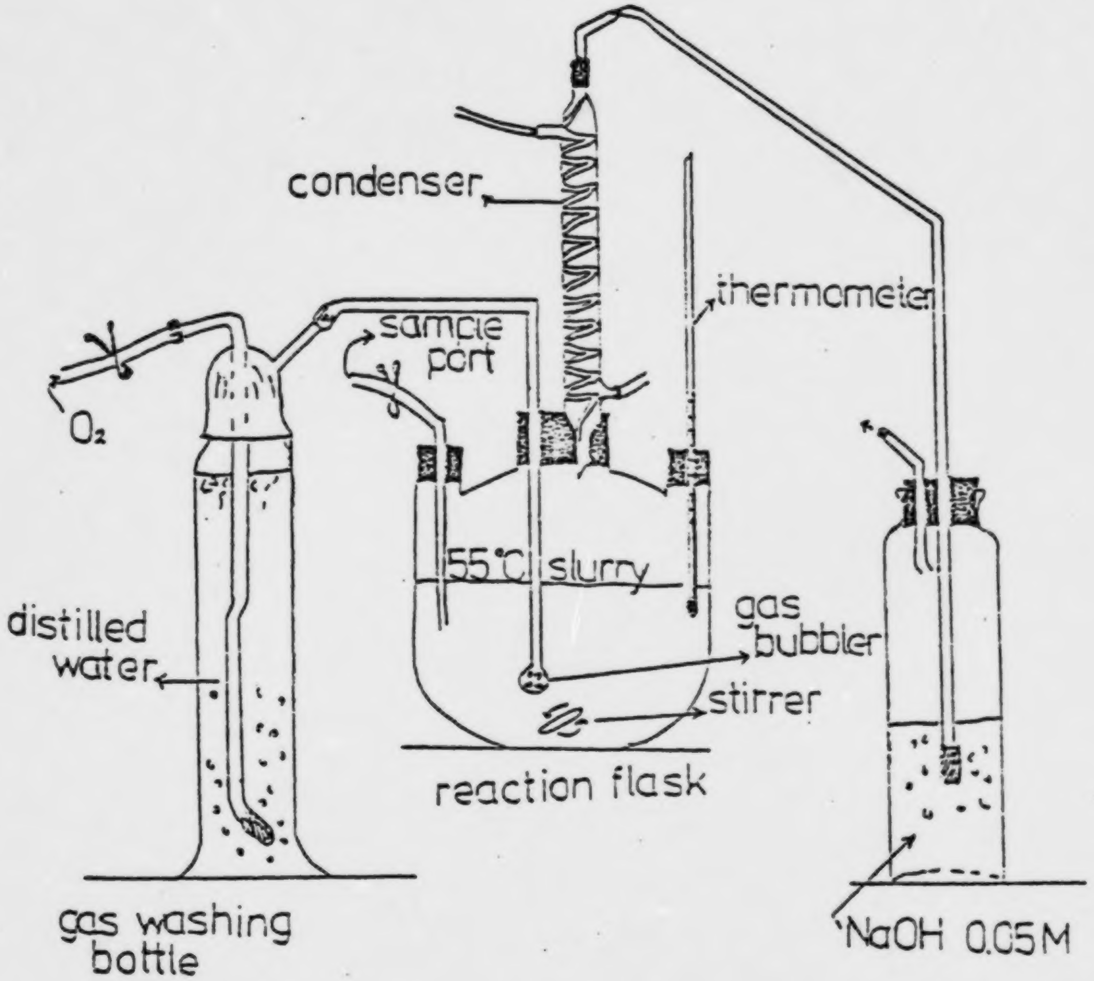

condenser
thermometer
sample port
O_2
55°C slurry
gas bubbler
distilled water
stirrer
reaction flask
gas washing bottle
NaOH 0.05M

Figure 3-5. Closed Glass Reactor (Garcia, 1980)

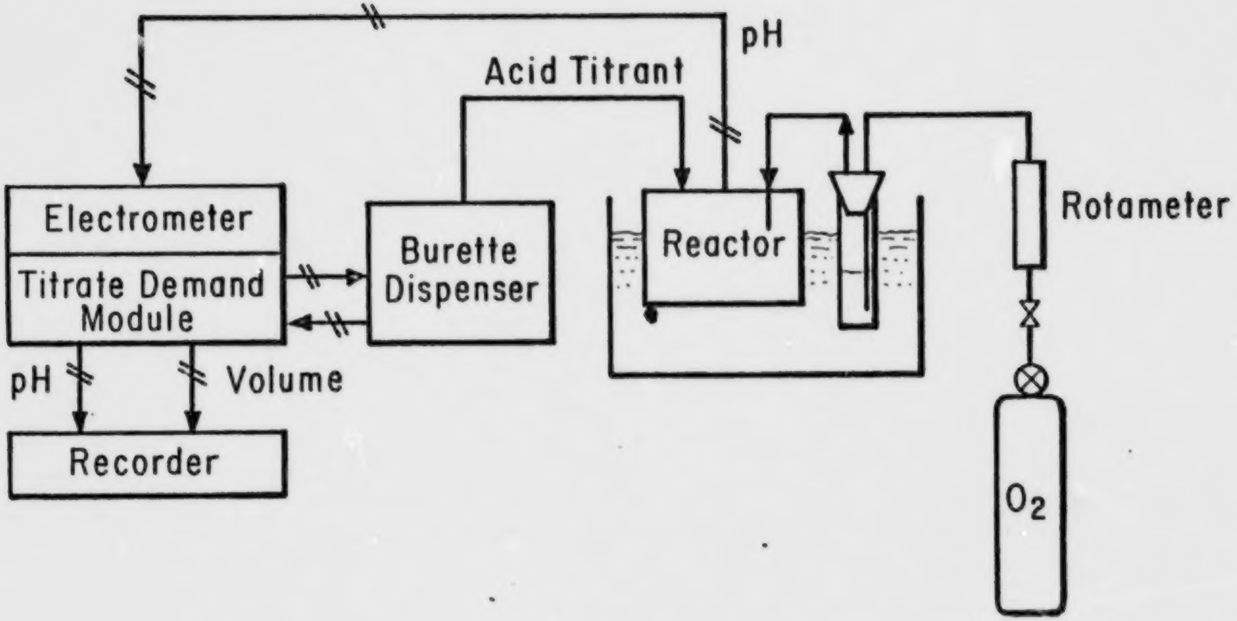

pH
Acid Titrant
Electrometer
Titrate Demand Module
Burette Dispenser
Reactor
Rotameter
pH
Volume
Recorder
O_2

Figure 3-6. pH-Stat Apparatus

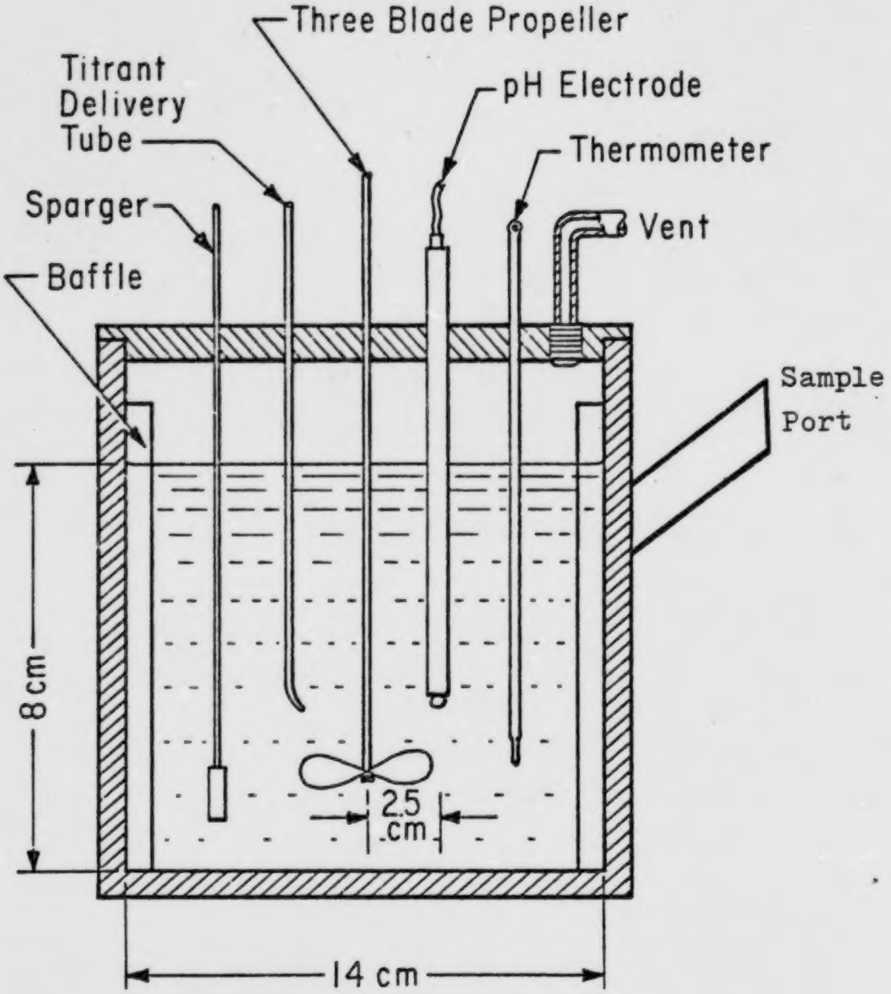

Three Blade Propeller
Titrant Delivery Tube
pH Electrode
Thermometer
Sparger
Vent
Baffle
Sample Port
8cm
2.5 cm
14 cm

Figure 3-7. Plexiglass Reactor

The pH of the slurry was measured at all times by a combination electrode calibrated at 55°C with standardized pH 4 phthalate and pH 7 phosphate buffers. The pH electrode was connected to the Fisher Titrimeter II Titration System, which consisted of a 10 ml burette dispenser, an electrometer, and a titrate demand module. The titrate demand module acted as a remote automatic on/off controller for the burette dispenser. Before the experiment the operating pH was set by the titrate demand module as a titration endpoint. When a pH increase above the endpoint was detected, an amount of 3N or 10N sulfuric acid was released by the burette dispenser to neutralize the slurry and restore the initial pH. The acid was added through a slanted glass-delivery tube. However, when the pH of the slurry dropped below that of the endpoint, the pH could not be controlled.

The reactor was immersed in a water bath maintained at 55 ±2°C with a mercury on/off thermoregulator actuating an electric heating coil. The temperature of the reacting slurry increased 10-20°C during most of the runs, because the poor conductivity of the plexiglass did not permit effective removal of heat generated by sulfite oxidation.

Pure oxygen gas controlled by a rotameter at 100 to 130 ml/hr was presaturated with water at 55°C before being sparged into the reactor.

EXPERIMENTAL PROCEDURES

The amount of chemical required for each experiment was weighed out on a Mettler balance (accuracy ±0.001 g). The chemicals were poured into a large beaker and dissolved in a liter of distilled water. The slurry was agitated for approximately twenty minutes, then was preheated to 55°C. Before the experiment, the oxygen flowrate was adjusted to give 100 to 200 ml/hr. The variable speed agitator was set at 950 rpm or 1340 rpm. The desired initial pH at 55°C was obtained by adding 10 N sulfuric acid or 5 N sodium hydroxide. After the pH of the solution stabilized, the experiment was started by simultaneously inserting the oxygen tube into the slurry and turning on the automatic burette dispenser. Reaction time was measured by a stop watch. The temperature of the slurry was periodically recorded. During each experiment eight slurry samples were taken and analyzed for total sulfite concentration by iodine titration. The slurry samples were then filtered and stored for carboxylic acid analyses by IC or ICE.

ANALYTICAL METHODS

Iodine Titration

The slurry samples collected during each experiment were analyzed for their sulfite concentration by iodine titration. One milliliter of the slurry sample was dissolved in approximately 30 ml of pH 6 acetate buffer solution. A known amount of excess iodine was determined by titration with standard sodium thiosulfate using starch as an endpoint indicator.

All samples were titrated at pH 4.0 to 8.0. Above pH 8.0, iodate (IO_3^-) is formed and reacts with thiosulfate to give sulfate rather than tetrathionate. Below pH 4.0, iodine oxidation by air and starch decomposition can affect the analysis.

Appendix 3-C gives the procedures of iodine titration and methods of calculating the total sulfite concentration and preparing the pH 6 acetate buffer solutions.

Ion Chromatography

A Dionex Model 14 Ion Chromatograph was used to determine adipic acid in experiments A4 through A8-3. The system used a 3 x 150 mm anion precolumn in series with a 3 x 500 mm anion separator column and a 6 x 250 mm suppressor column. A mixture of sodium carbonate and sodium bicarbonate solution was used as eluent. The eluent strength varied from 2.4 mM $NaCO_3$/3.0 mM $NaHCO_3$ to 1.6 mM Na_2CO_3/2.0 mM $NaHCO_3$. The flow rate of the eluent was maintained constant at 138 ml/min. With this system, it is not possible to separate glutaric and adipic acids. Valeric acid came out early and was not easily resolved from chloride.

A brief theory of IC and a short section on IC solution preparation and typical IC results are given in Appendix 3-D.

Ion Chromatography Exclusion

A Dionex Model 14 Ion Chromatograph was used to analyze adipic acid and its degradation products by ion chromotography exclusion (ICE). The system used a 9 x 250 mm separator column and a 4 x 280 mm suppressor column. The eluent was 0.02 to 0.1 mM hydrochloric acid at 46 to 62.6 ml/hr. To get reproducible results, the system was calibrated with adipic acid standards before each analysis. A mixture of 0.05 to 0.1 mM of succinic, adipic, and glutaric acids was separated successfully on the ICE using 0.1 mM HCl as the eluent. Varleric acid could not be analyzed because its extremely long elution time (40 minutes) results in a very broad peak.

The theory of ICE, method of ICE solution preparation, and typical ICE results are given in Appendix 3-E.

Total Carbon Analyzer

An Oceanography 525 Carbon Analyzer was used to measure carbon concentration in filtered solution. Liquid samples were injected into the sample filament where organic materials were oxidized to carbon dioxide by pure oxygen with the aid of catalyst. The catalyst in the sample filament consisted of asbestos, cobalt nitrate, and manganese dioxide. The cobalt allows the asbestos to hold up under heat for longer periods of time and the manganese dioxide is an oxidation catalyst. The CO_2 formed in the furnace was detected with a Horiba PIR-2000 CO_2 analyzer. Adipic acid was used to prepare the standard solution for calibration.

Gas Chromatography

A Varian 3700 Gas Chromatograph with a flame ionization detector was used to analyze adipic acid and its degradation products. A 6 ft, ¼-inch glass column packed with 100/120 chromasorb, 10 percent SP-1000, 1 percent H_3PO_4 was used for both mono- and dicarboxylic acids. For dicarboxylic acid analyses, the aqueous sample was esterified with methanol in 50% H_2SO_4, and then extracted with chloroform. For monocarboxylic acid analyses, no esterification was needed. The sample was extracted with chloroform after acidification. Supelco volatile and nonvolatile acid standards were used for calibration. The flow rates in this system were He: 30 ml/min, H_2: 28.6 ml/min and air: 150 ml/min. Detailed analytical procedures and typical GC results are given in Appendix 3-G.

Gas Chromatograph-Mass Spectrometer

A Finnigan 4023 Gas Chromatograph-Mass Spectrometer (GC/MS) with INCOS Data System was used to identify degradation products of adipic acid.

The analytical procedures were the same as those for gas chromatography alone. The separation column had the same packing but different shape (required to fit Finnigan 4023 GC/MS).

CHAPTER 3-4

RESULTS AND DISCUSSION

SUMMARY

The rate of adipic acid degradation was found to be directly proportional to the rate of sulfite oxidation and the adipic acid concentration. The proportionality constant, k_d, was used to correlate degradation data in this work with laboratory measurements at Radian and pilot plant results from Research Triangle Park and Shawnee. Table 3-2 summarizes all the results.

The rate of sulfite oxidation, in the absence of Mn^{++}, is strongly pH dependent and decreases as pH increases. The oxidation is catalyzed by Mn^{++} and inhibited by thiosulfate and hydroxycarboxylic acids. In the presence of 1.0 mM Mn^{++}, the oxidation rate is pH independent and is probably controlled by mass transfer. Thiosulfate has a threshold effect on sulfite oxidation in the presence of 1.0 mM Mn^{++}, and the threshold concentration is pH dependent.

The degradation rate constant increases as pH increases. Mn at 0.3 to 1.0 mM strongly inhibits the degradation. The inhibition is more effective at low pH. Degradation can be reduced by high dissolved sulfite concentration induced by excess sulfate ions. Hydroxycarboxylic acids with concentrations greater than 10 mM do not degrade even with sulfite oxidation catalyzed by Mn. Thiosulfate tends to inhibit degradation at high pH in the presence of Mn^{++}. The degradation rates of Monsanto dibasic acid are similar to those of adipic acid.

Glutaric, succinic, malonic, valeric and butyric acids were identified as degradation products. 4-carboxybutanal was the major degradation product in the absence of Mn^{++} while glutaric acid is the major product in the presence of 1.0 mM Mn^{++}. Around 40% of the degradation products (probably CO_2 gas) are still not measurable.

SULFITE OXIDATION

The rate of sulfite oxidation was a function of agitation rate, oxygen

Table 3-2: Oxidative Degradation of Carboxylic Acids

Run	pH	Other Component[a] (mM)	Sulfite Oxidation Rate (M/hr)	Degradation[b] Rate Constant, k_d (M^{-1})
Glass Reactor, 110 ml/min O_2, 500 ml slurry				
Sulfosuccinic (SS)				
SS1	5.0+	-	0.07	1.0
Sulfopropionic (SP)				
SP1	5.0+	-	0.07	1.0
Adipic (A)				
A1	5.0+	-	0.06	1.5
A4	4.3+	-	0.04	1.1
A5	5.0+	-	0.04	1.7
Plexiglass reactor, 110 ml/min O_2, 950 rpm, 1 L slurry				
A7	4.3	1 Fe	0.46	1.2
A81[c]	5.0	0.1+ Mn	0.37	0.3
A82	5.0	-	0.38	2.0
A83[c]	5.0	0.1+ Mn	0.35	0.4
A9	5.0	300 Na_2SO_4	0.44	0.3
A10	4.3	1 Fe, 1 Mn	0.38	0.3
A11	6.0	-	0.0	-
Plexiglass reactor, 200 ml/min O_2, 1340 rpm				
A12	4.3	-	0.64	0.7
A13	4.3	1 Mn	0.67	0.1
A14	5.0	-	0.08	1.4
A15	5.0	1 Mn	0.68	0.2
A16	5.5	1 Mn	0.67	0.6
A17	4.7	1 Mn	0.70	0.2
A18	5.0	-	0.20	1.4
A19	5.5	-	0.13	1.3
A20	5.0	300 $CaCl_2$	0.45	1.1
A21	5.0	5A	0.26	1.6
A22	5.0	300 $MgSO_4$	0.36	0.6
A23	5.0	1 Mn, 20A	0.78	0.3
A24	4.3	-	0.61	0.6
A25	5.0	0.1 Mn	0.62	1.3
A26	5.5	1 Mn	0.96	0.2
AA1	5.5	1 Mn	0.33	0.6
AA2	5.5	1 Mn, 10 HA	0.23	0.5
AA3	4.5	1 Mn, 10 HA	0.55	0.1
AA4	4.5	1 $Na_2S_2O_3$	0.01	0.1
Glutaric acid (G)				
G1	4.6	-	0.42	0.3

Table 3-2 (continued)

Run	pH	Other Component[a] (mM)	Sulfite Oxidation Rate (M/hr)	Degradation[b] Rate Constant, k_d (M^{-1})
Succinic (S)				
S1	4.5	-	0.56	0.5
S2	4.5	1 Mn	0.69	0
S3A	5.5	-	0.06	5
S3B	5.5	1 Mn, 6.3 S	0.38	0.2
S4	4.5	0.33 Mn	0.41	0
S5	4.4	0.1 Mn	0.54	0.5
β-Hydroxypropionic (HP)				
HP1	4.5	2 HP	0.52	0.2
HP2	4.5	1 Mn	0.49	0.1
HP3	4.5	25 HP	0.06	-
HP4	5.5	25 HP, 1 Mn	0.57	0
HP5	4.5	-	0.06	-
Hydroxyacetic (HA)				
HA1	4.5	-	0.04	-
HA2	5.5	1 Mn	0.74	0
HA3	5.0	-	0.02	-
HA4	5.0	0.1 Mn	0.06	-
HA5	5.0	0.3 Mn	0.37	0.1
AA2	5.5	1 Mn, 10 A	0.23	0
AA3	4.5	1 Mn, 10 A	0.55	0
Fumaric (F)				
F1	5.5	1 Mn	0.21	2.4
Monsanto Dibasic Acid (M)				
M1	5.5	1 Mn	0.25	0
M2	5.5	1 Mn, 1 $Na_2S_2O_3$	0.38	0
M3	4.0	-	0.51	0.05
M4	5.0	-	0.19	0.6
Plexiglass reactor, 130 ml/min O_2, 1340 rpm				
Adipic Acid				
AA5	4.5	1 Mn, 1 $Na_2S_2O_3$	0.42	0.1
AA6	5.0	0.3 $MgSO_4$, 1 $Na_2S_2O_3$	0.36	0.1
AA7	5.0	0.3 $MgSO_4$, 10 $Na_2S_2O_3$	0.0	-
AA8	5.0	0.3 $MgSO_4$, 10 $Na_2S_2O_3$, 1 Mn	0.44	0.2
AA9	5.5	1 Mn, 10 $Na_2S_2O_3$	0.0	-
AA10	5.0	1 Mn, 10 $Na_2S_2O_3$	0.0	-
AA11	4.5	1 Mn, 10 $Na_2S_2O_3$	0.0	-
AA12	5.5	1 $Na_2S_2O_3$	0.08	-
AA13	5.5	1 Mn, 1 $Na_2S_2O_3$	0.50	-

Table 3-2 (continued)

Run	pH	Other Component[a] (mM)	Sulfite Oxidation Rate (M/hr)	Degradation[b] Rate Constant, k_d (M^{-1})
(Adipic Acid)				
AA14	5.5	1 Mn, 1 $Na_2S_2O_3$	0.0	-
AA15	5.0	1 Mn, 3 $Na_2S_2O_3$	0.0	-
AA16	4.5	1 Mn, 3 $Na_2S_2O_3$	0.45	0.1
AA17	5.5	1 Mn, 2 $Na_2S_2O_3$	0.0	-
AA18	5.0	1 Mn, 2 $Na_2S_2O_3$	0.52	0.2
AA19	5.5	1.2 Mn, 1.2 $Na_2S_2O_3$	0.45	0.2
AA20	5.5	1 Mn, 0.5 $Na_2S_2O_3$	0.50	0.3
AA21	5.5	0.1 Mn	0.31	1.8
AA22	5.5	3 Mn	0.47	0.1
AA23[d]	5.5	3 Mn	0.46	0.4
Succinic Acid				
S6	4.5	0.2 Mn	0.30	0.4
Glutaric Acid (G)				
G3	5.5	-	0.01	-
G4	5.5	0.1 Mn	0.30	1.6

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[a] Initial carboxylic acid concentration is 10 mM unless noted

[b] $k_d = d \ln[\text{acid}]/d\ [SO_3^{=}]_T$

[c] These runs used purchased $CaSO_3$ with Mn impurities

[d] This run used slurry from AA22 with added calcium sulfate

flow rate, pH, catalyst concentration, and inhibitor concentration. Mn^{++}, Fe^{++}, and $SO_4^=$ were found to be catalysts while thiosulfate ($S_2O_3^=$) and hydroxycarboxylic acids were inhibitors. Agitation and oxygen flow rate affect the mass transfer of reactants and products through the reaction boundary layer.

Typical sulfite oxidation behavior at 1340 rpm is shown in Figures 3-8 and 3-9 for two different batches of calcium sulfite prepared in the lab. Both figures indicate that the sulfite oxidation rate is rather constant throughout the experiment in the presence of a high concentration of Mn^{++} (1.0 mM) which acts as a catalyst. In the absence of Mn^{++} or other added catalysts the sulfite oxidation rate increases or decreases during the experiment, depending on the concentration change of catalysts and inhibitors. The catalysts and inhibitors could be released during the dissolution of calcium sulfite or reduced by coprecipitation with calcium sulfate. In addition, dicarboxylic acids are mild inhibitors. Therefore, the sulfite oxidation rate increased or decreased, depending on which effect was stronger.

In the presence of 1.0 mM Mn^{++}, sulfite oxidation with 200 ml/min oxygen at 1340 rpm agitation was not a function of pH. Figure 3-10 shows that the sulfite oxidation rate under the conditions described above was 0.67 M/hr. The reaction rate was mass transfer controlled and was limited by the combination of agitation and oxygen flow rate. Without Mn^{++} (Figure 3-11), the sulfite oxidation rate decreased as pH increased (Table 3-2, Runs A12, A18, and A19). The sulfite oxidation rate, in the absence of Mn^{++} or other catalysts, was kinetically controlled. In the absence of Mn^{++}, the oxidation rate is given approximately by

$$R = 1.1 \times 10^4 \, [H^+]^{1.0}$$

where R is the sulfite oxidation rate in units of M/hr and $[H^+] = 10^{-pH}$.

High sulfite concentration induced by addition of 0.3 M Na_2SO_4 or $MgSO_4$ at pH 5.0 had no effect on the oxidation rate at 950 rpm agitation (Table 3-2, Runs A32 and A9), but increased the rate from 0.2 to 0.36 M/hr at 1340 rpm (Table 3-2, Runs A18, A22). In the presence of 1.0 mM thiosulfate, an inhibitor to sulfite oxidation, and 0.3 M $MgSO_4$, the oxidation rate at pH 5.0 was 0.36 M/hr while the oxidation rate at pH 4.5, in the presence of 1.0 mM

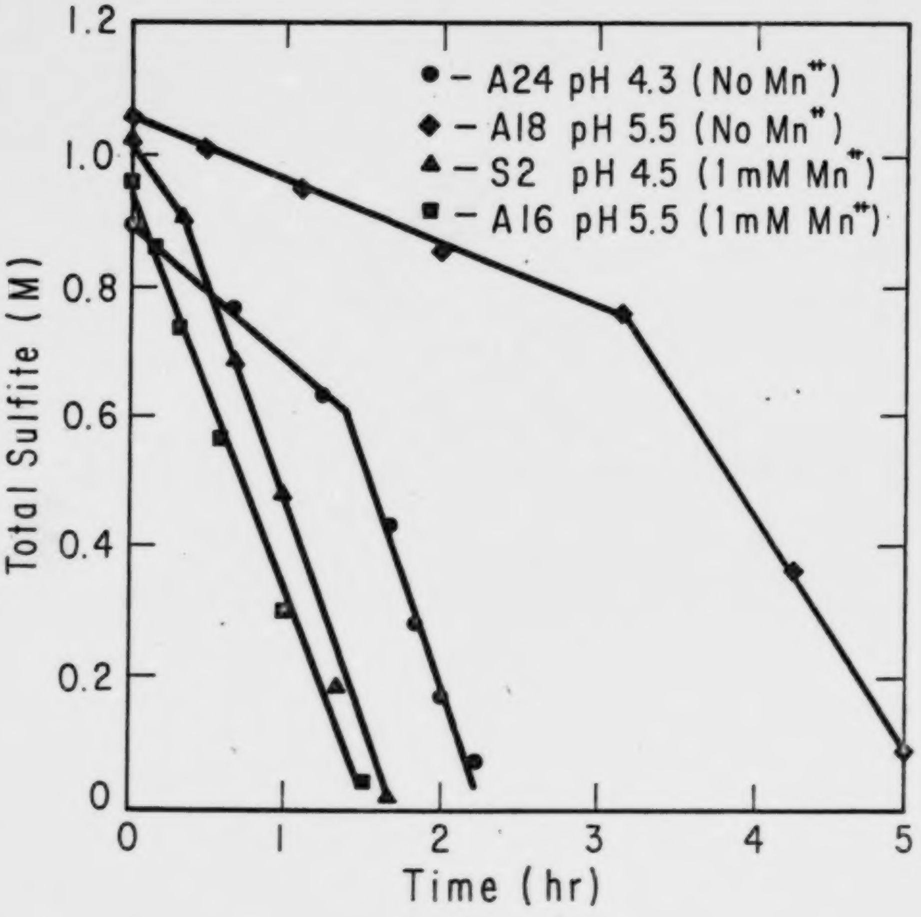


Figure 3-8 Oxidation of Calcium Sulfite - Batch I

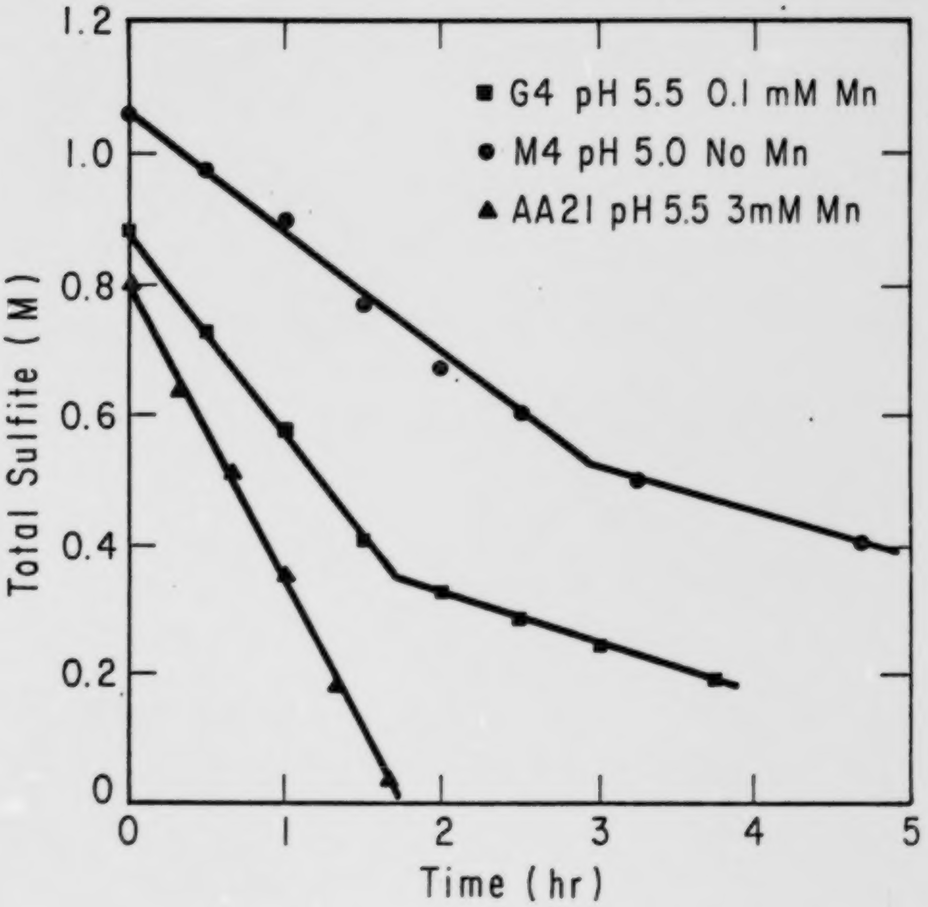


Figure 3-9 Oxidation of Calcium Sulfite - Batch II

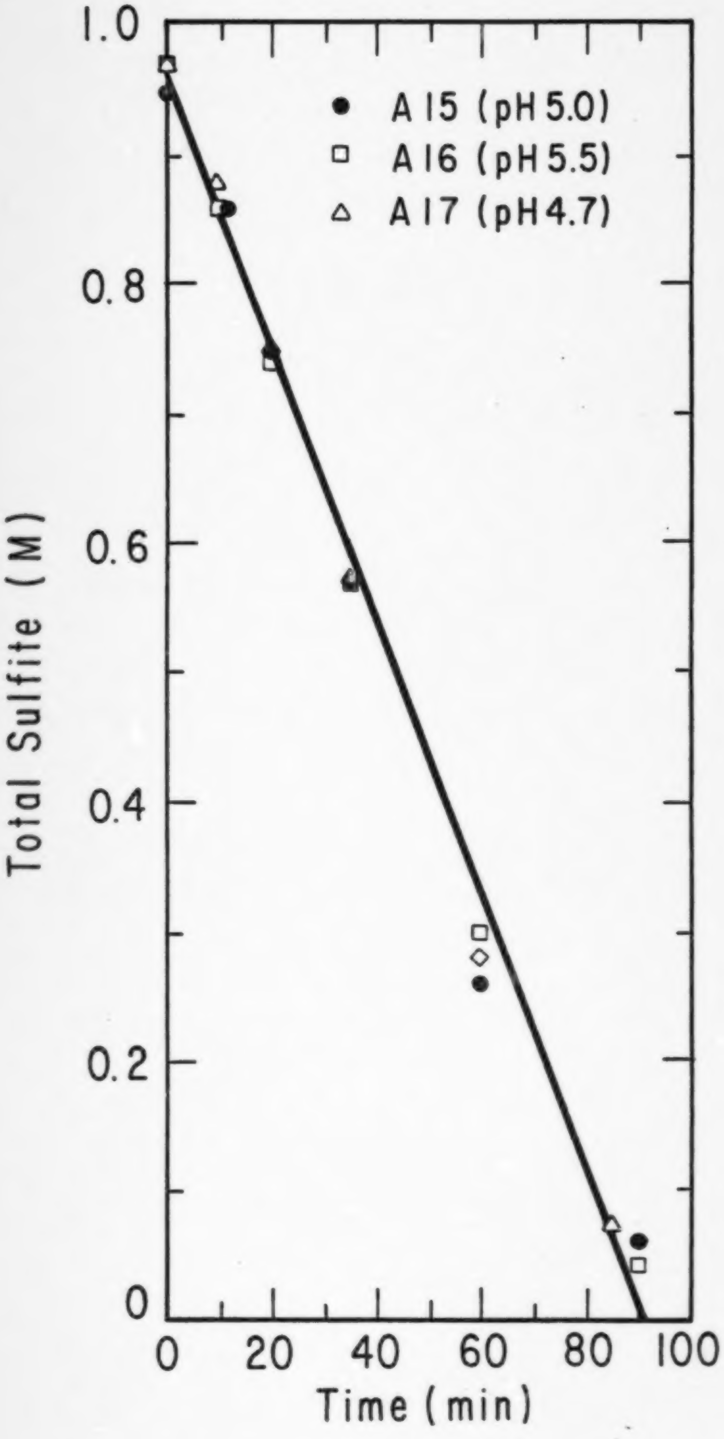


Figure 3-10 Sulfite Oxidation with 1.0 mM Mn^{++}, with 200 ml/min O_2 at 1340 rpm agitation.

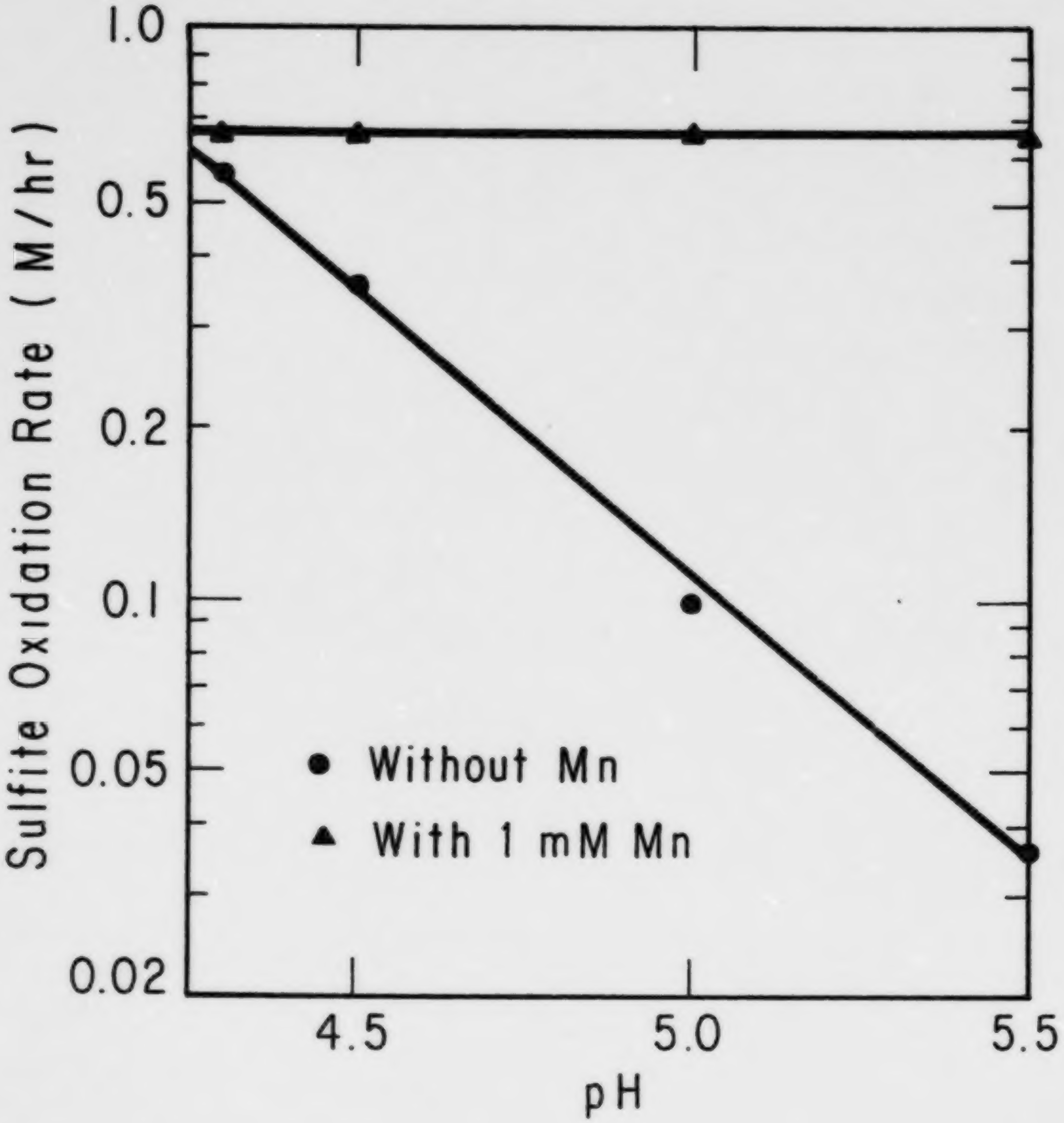


Figure 3-11. Effect of pH on Sulfite Oxidation 1340 rpm, 200 ml O_2/min.

thiosulfate without $MgSO_4$, is almost zero (Table 3-2, AA6, AA4). The addition of sulfate increased the dissolved sulfite concentration by the sulfite-sulfate equilibrium and therefore increased the sulfite oxidation rate:

$$CaSO_3(s) + SO_4^{=} \rightleftarrows CaSO_4(s) + SO_3^{=}$$

Thiosulfate was found to be powerful inhibitor. In the absence of Mn^{++}, 1 mM Na_2SO_3 was sufficient to inhibit sulfite oxidation even when the pH was as low as 4.5 (Table 3-2, AA4). It appears that thiosulfate has a threshold effect on sulfite oxidation and the threshold concentration of thiosulfate in the presence of 1 mM Mn^{++} decreases as the pH increases (Figure 3-12).

It was found that hydroxycarboxylic acids were inhibitors of sulfite oxidation, β-hydroxypropionic acid inhibited the oxidation when its concentration was 10 mM or higher. When the concentration of hydroxypropionic acid was as low as 2 mM, the sulfite oxidation was unaffected.

Inhibition of β-hydroxypropionic acid was compensated for by 1.0 mM Mn^{++} even when the acid concentration was as high as 25 mM (Table 3-2, HP). Hydroxyacetic acid shows the same effect as β-hydroxypropionic acid (Table 3-2, HA). Figure 3-13 shows that 0.3 mM Mn was sufficient to compensate for 10 mM hydroxyacetic acid at pH 4.5.

The rate of oxidation in the glass reactor was 0.04 M/hr at pH 4.3-5.0, lower than that obtained by Radian in a similar glass reactor, 0.08 M/hr.

Addition of $CaCl_2$ should reduce oxidation by suppressing total dissolved sulfite:

$$CaSO_3 + H^+ \rightleftarrows Ca^{++} + HSO_3^-$$

However, the rate was increased possibly due to change in the bubble size affected by $CaCl_2$ or to the introduction of catalyst impurities with the $CaCl_2$.

ADIPIC ACID DEGRADATION RATES

A rate expression for adipic acid degradation was proposed by Rochelle (Meserole et al., 1980).

$$\frac{d[A]}{dt} = k_d \frac{d[SO_3]^{=}}{dt}[A]$$

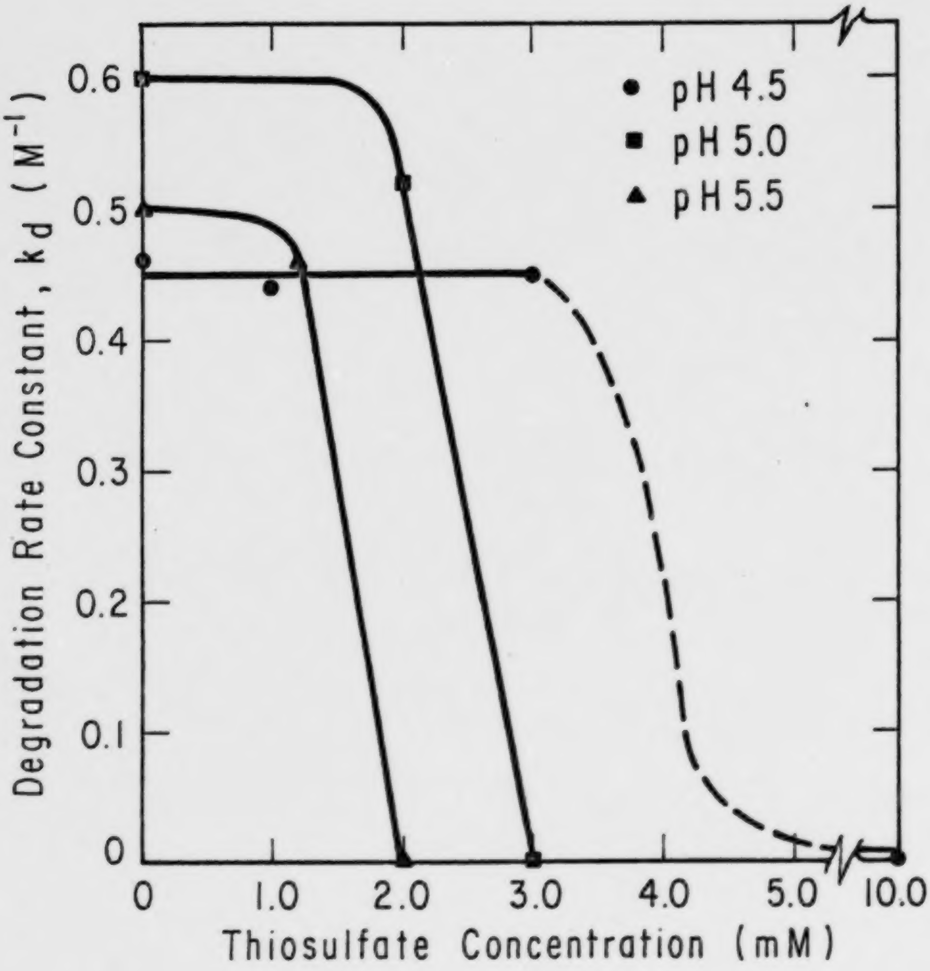


Figure 3-12. Effect of Thiosulfate on Adipic Acid Degradation, 1.0 mM Mn

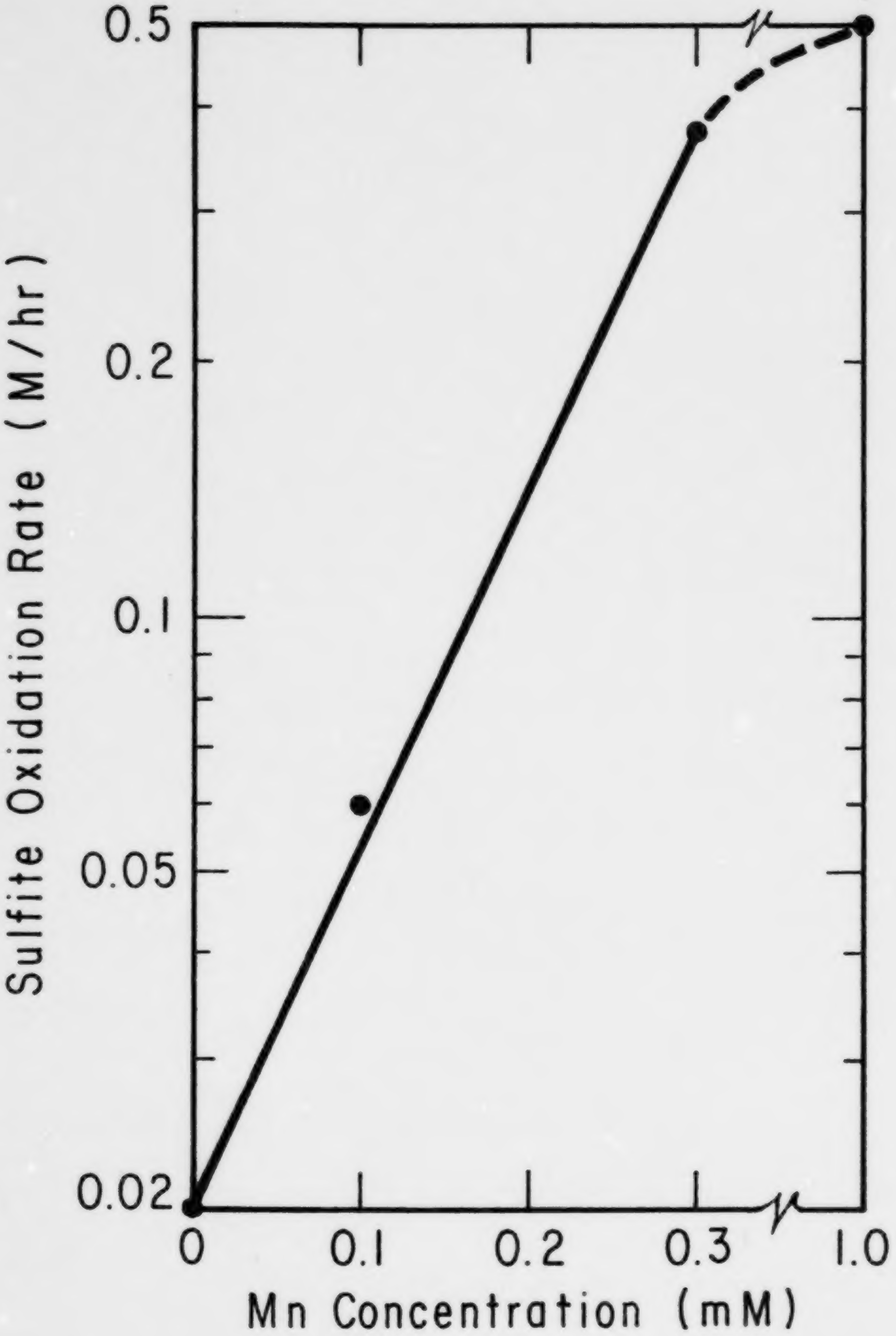


Figure 3-13. Effect of Mn on Sulfite Oxidation with 10 mM Hydroxyacetic acid, pH 4.5.

Eliminating time and integrating the differential equation give:

$$\ln[A] = k_d[SO_3^=] + C$$

The degradation rate constant, k_d, is obtained as the slope of a plot of ln [A] versus $[SO_3^=]$. Typical plots of ln [A] versus $[SO_3^=]$ are shown in Figure 3-14 for slow degradation in A12 at pH 4.3 and fast degradation in A18 at pH 5.0. The degradation rate constants of these two runs were 0.7 and 1.4 M^{-1}, respectively.

From the straight line plot of ln [A] versus $[SO_3^=]$, as shown in Figure 3-14, the adipic acid degradation reaction is apparently proportional to the first order of adipic acid concentration. In addition, the first order dependence on adipic acid concentration was confirmed by a series of experiments made at pH 5.0 with initial adipic acid concentrations between 5 and 20 mM. In A15 and A23 with 1 mM Mn^{++}, initial adipic acid concentrations were 10 mM and 20 mM, respectively, and k_d was 0.2 M^{-1} and 0.3 M^{-1}, respectively. In A18 and A14, without Mn^{++}, the initial adipic acid concentrations were 10 mM and 5.0 mM, respectively, and k_d was 1.4 M^{-1} and 1.6 M^{-1}, respectively.

Figure 3-15 gives k_d as a function of pH with and without Mn^{++} at 1340 rpm in the plexiglass reactor. It was found that 0.1-1.0 mM Mn^{++} effectively inhibits adipic acid degradation during sulfite oxidation. Mn^{++} inhibits degradation more effectively at low pH and less effectively at high pH. The effect of pH on k_d is greater with Mn^{++} than without. Without Mn^{++}, k_d is given by the empirical relationship:

$$k_d = 3.5 \times 10^{-2}[H^+]^{-0.3}$$

With 0.3 to 1.0 mM Mn^{++}, k_d is given by:

$$k_d = 3.5 \times 10^{-4}[H^+]^{-0.6}$$

Mn^{++} was initially identified as a degradation inhibitor in A8-1 with purchased $CaSO_3$ solids. Analysis of the solution from this experiment by atomic absorption spectrophotometry gave 0.1 mM Mn and no Fe in the initial sample. No Fe or Mn was found in samples from A8-2, A12 and A14 with synthesized $CaSO_3$. Since Fe was confirmed in A7 as having no effect on degradation, Mn must have been responsible for inhibiting degradation in A8-1.

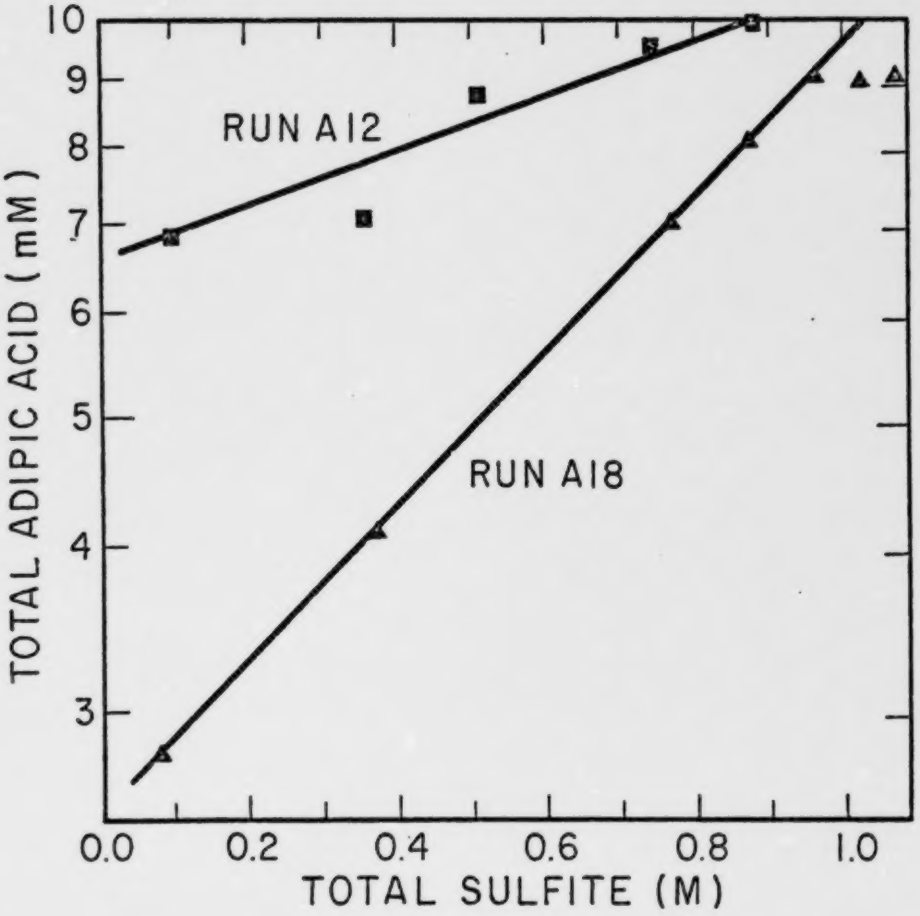


Figure 3-14. Adipic Acid Concentration as a Function of Total Sulfite Concentration, Run A12 at pH 4.3, Run A18 at pH 5.0

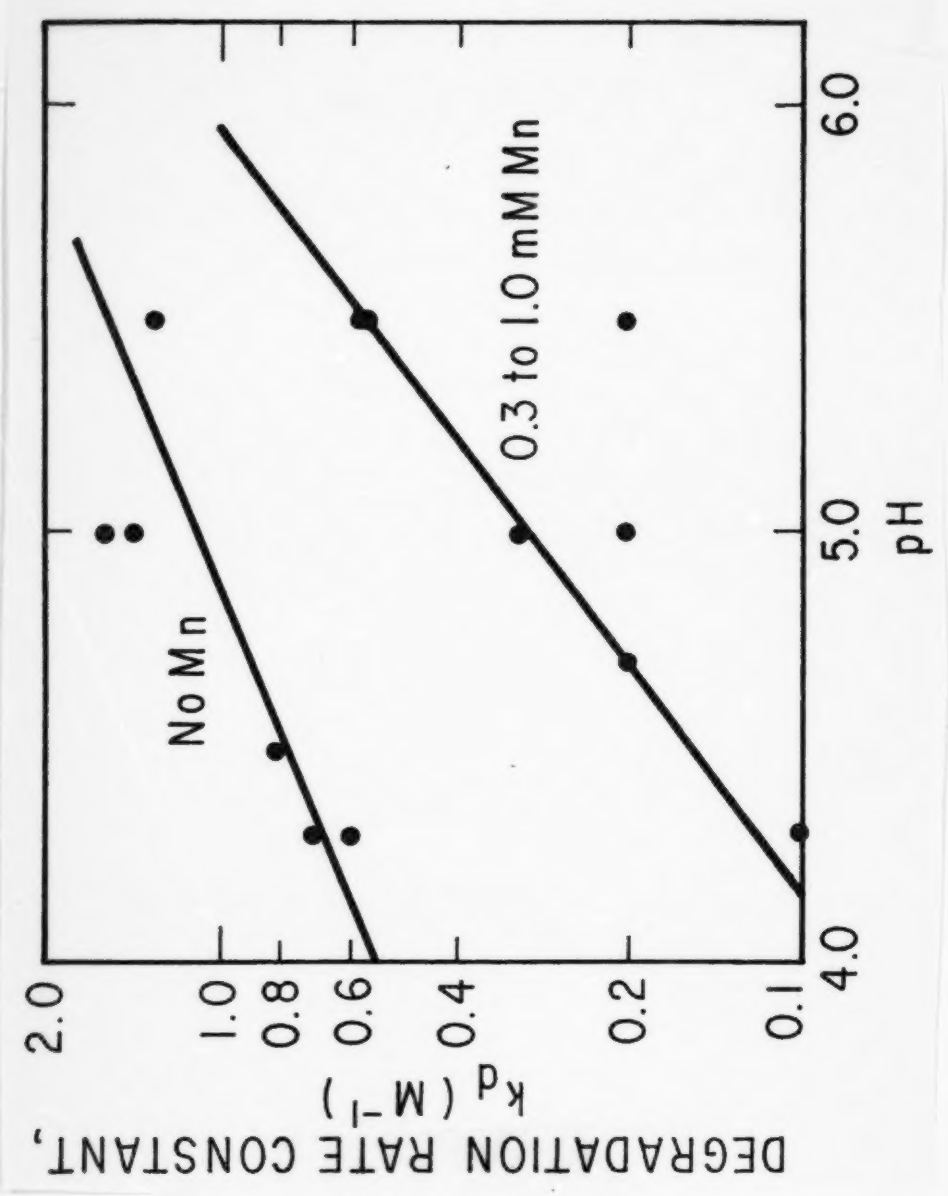


Figure 3-15. Adipic Acid Degradation in Plexiglass Reactor at 1340 rpm

A series of experiments using succinic acid as buffer additive were used to investigate the Mn^{++} effect on oxidative degradation of dicarboxylic acid. The data are shown in Figure 3-16. It was found that 0.2 mM or less Mn^{++} had only a small effect on degradation, while 0.3 mM Mn^{++} almost completely inhibited degradation. More concentrated Mn^{++} had no additional measurable effect on the degradation rate.

Atomic absorption analyses of initial, intermediate, and final solutions from A13, A15, A16 and A17 at pH 4.3 to 5.5 with nominal concentration of 1 mM Mn^{++} gave actual concentrations of 0.8 to 1.0 mM. Therefore, the pH effect in the presence of Mn^{++} was not caused by lower Mn^{++} solubility at high pH. A possible explanation for the effect of Mn^{++} is that it inhibits adipic acid degradation by altering the sulfite oxidation mechanism and resulting in a lower free radical concentration available for attacking adipic acid.

Runs A9 and A22 (Table 3-3) showed that degradation can be reduced by high dissolved sulfite concentration induced by excess sulfate ions:

$$CaSO_3(s) + SO_4^{=} \longrightarrow CaSO_4(s) + SO_3^{=}$$

At a given sulfite oxidation rate, a higher level of dissolved sulfite should give a lower concentration of free radical for attacking adipic acid. A19 and A20 had higher rates of adipic acid degradation near completion of the sulfite oxidation, probably due to decreased dissolved sulfite.

Hydroxycarboxylic acids were found to inhibit sulfite oxidation. Since the degradation of carboxylic acid was conjugated with sulfite oxidation, the carboxylic acid did not degrade to any degree if sulfite was not oxidized. Addition of 0.3 mM Mn^{++} with the hydroxy acids compensated for the inhibition and results in a significant amount of sulfite oxidation. Even with sulfite oxidation, hydroxyacetic acid did not degrade to any significant extent when its nominal concentration was 10 mM. When the concentration was reduced to 2.0 mM the degradation rate constant was found to be 0.37 M^{-1} at pH 5.5 (Table 3-2, HA6). β-hydroxypropionic acid had the same behavior as hydroxyacetic acid (Table 3-2, HP). From these two series of experiments we conclude that (1) hydroxycarboxylic acids inhibit sulfite oxidation, but this inhibition can be compensated for by adding 0.3 mM or more Mn^{++}, (2) hydroxycarboxylic acids are not degraded if their concentration is above 10 mM.

Thiosulfate was found to be a powerful inhibitor of sulfite oxidation.

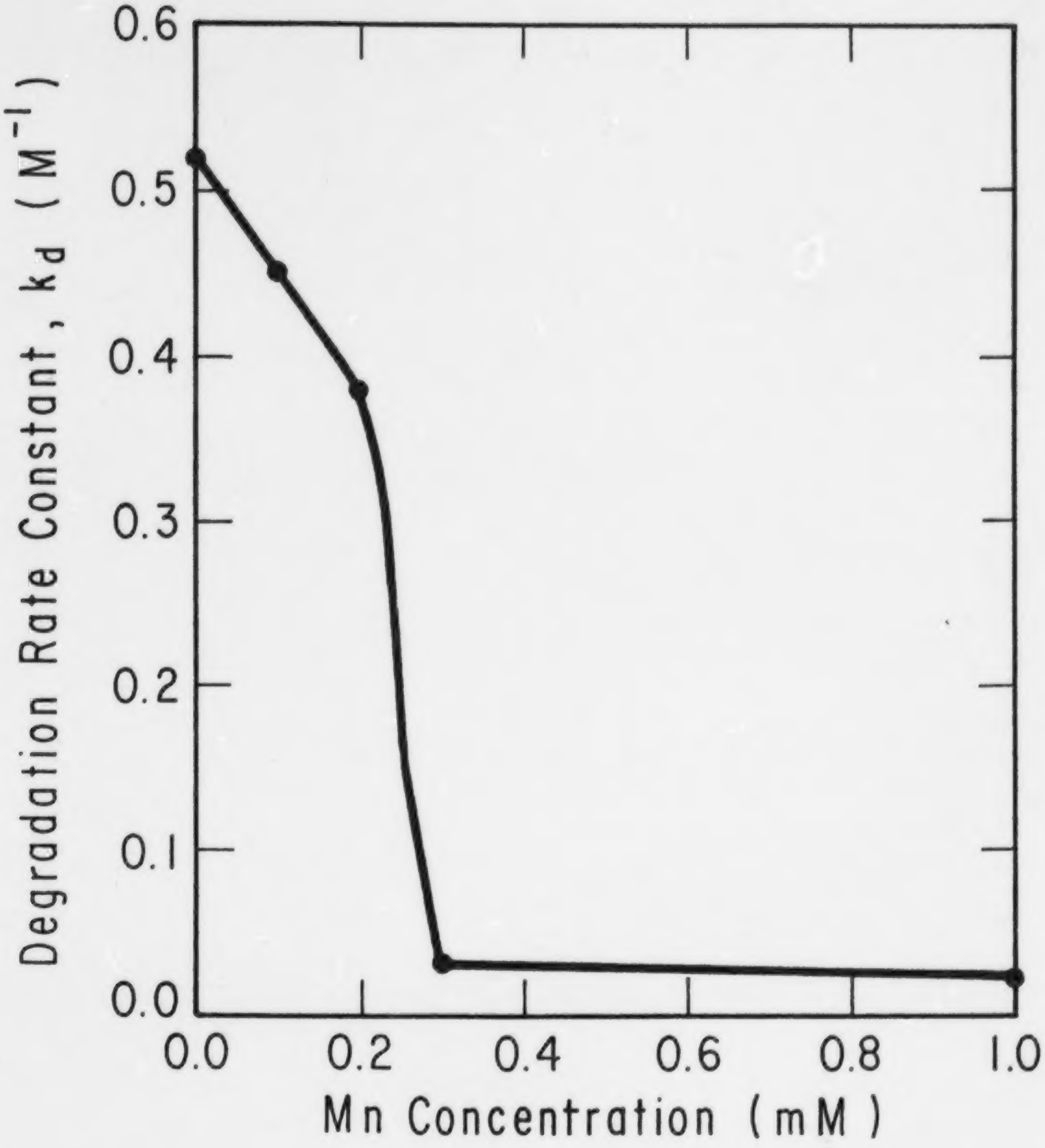


Figure 3-16. Effect of Mn on Succinic Acid Degradation at pH 4.5.

Table 3-3: Sulfite Effect on Degradation

Run	Agitator Speed (rpm)	pH	Other Component (mM)	Oxidation Rate (M/hr)	Degradation Rate, k_d (M^{-1})
A82	950	5.0		0.38	2.0
A9	950	5.0	300 Na_2SO_4	0.44	0.3
A18	1340	5.0		0.2	1.4
A22	1340	5.0	300 $MgSO_4$	0.36	0.6

Table 3-4: Carbon Balance Studies, Analyses by Gas Chromatography and ICE (noted by parentheses), concentrations as g C/liter

Sample	AA1	AA2	A19
Mn (mM)	1.0	1.0	0.0
Adipic	0.439 (0.266)	0.504 (0.302)	0.187 (0.144)
Glutaric	0.054	0.096	0.018
Succinic	0.014	0.014	0.010
Valeric	0.055	0.043	0.018
Hydroxyacetic	-	0.240 (0.204)	-
Total Identified	0.562 (0.389)	0.897 (0.659)	0.233 (0.190)
TOC, initial	0.62	0.96	0.59
TOC, final	0.49	0.71	0.43
Final TOC - Total Identified	-0.072 (0.101)	-0.187 (0.051)	-0.192 (0.240)
Percent of Degraded C as Volatiles	(36.7)	(55.1)	(35.9)

As mentioned in the section on sulfite oxidation, thiosulfate had a theshold effect on sulfite oxidation. When the thiosulfate concentration was above the threshold concentration, 1 mM Mn^{++} did not overcome inhibition caused by the presence of thiosulfate. In the presence of 1 mM Mn^{++}, when thiosulfate concentration is below its threshold concentration, the adipic acid degradation rate constant is independent of thiosulfate concentration at pH 4.5 and pH 5.0. The degradation rate constant is a stronger function of thiosulfate concentration at pH 5.5. It decreases as thiosulfate concentration increases. Therefore, thiosulfate tends to inhibit adipic acid degradation as shown in Figure 4-17. However, it seems that Mn^{++} and thiosulfate together have no additive effect on inhibiting adipic acid degradation.

Fumaric acid, an unsaturated dicarboxylic acid, had a very high degradation rate constant, possibly because of the presence of the unsaturated bond.

The degradation rates of Monsanto dibasic acid (DBA) are given in Table 3-2. This waste solid is primarily glutaric acid with some succinic and adipic acid. The degradation rate constant is based on the total concentration of succinic, glutaric, and adipic acid. The degradation rates are similar to those of adipic acid. Very little degradation was found at pH 4.0, even in the absence of Mn^{++}.

DEGRADATION PRODUCTS

Two sets of experiments were extensively analyzed for degradation products. Solutions from runs AA1, AA2 and A19 were analyzed in an attempt to close the carbon balance. Solutions from runs AA21, AA23, AA24, G3 and G4 were analyzed to identify and quantify degradation products as a function of run conditions.

Solutions from AA1, AA2 and A19 were analyzed by ion exclusion chromatography (ICE), gas chromatography (GC) and total carbon analyzer (TOC). The analytical results are given in Table 3-4. The quantitative analyses by GC were uniformly high and gave more carbon in the solution than measured by TOC in runs AA1 and AA2. ICE analyses were lower and more reasonable. The combination of adipic acid analyzed by ICE and other acids by GC accounted for all but 8 to 50% of the total carbon measured. The specific acids determined by GC accounted for 11 to 54% of the total carbon which was not adipic acid. The percent of degraded acid that was lost as volatiles varied

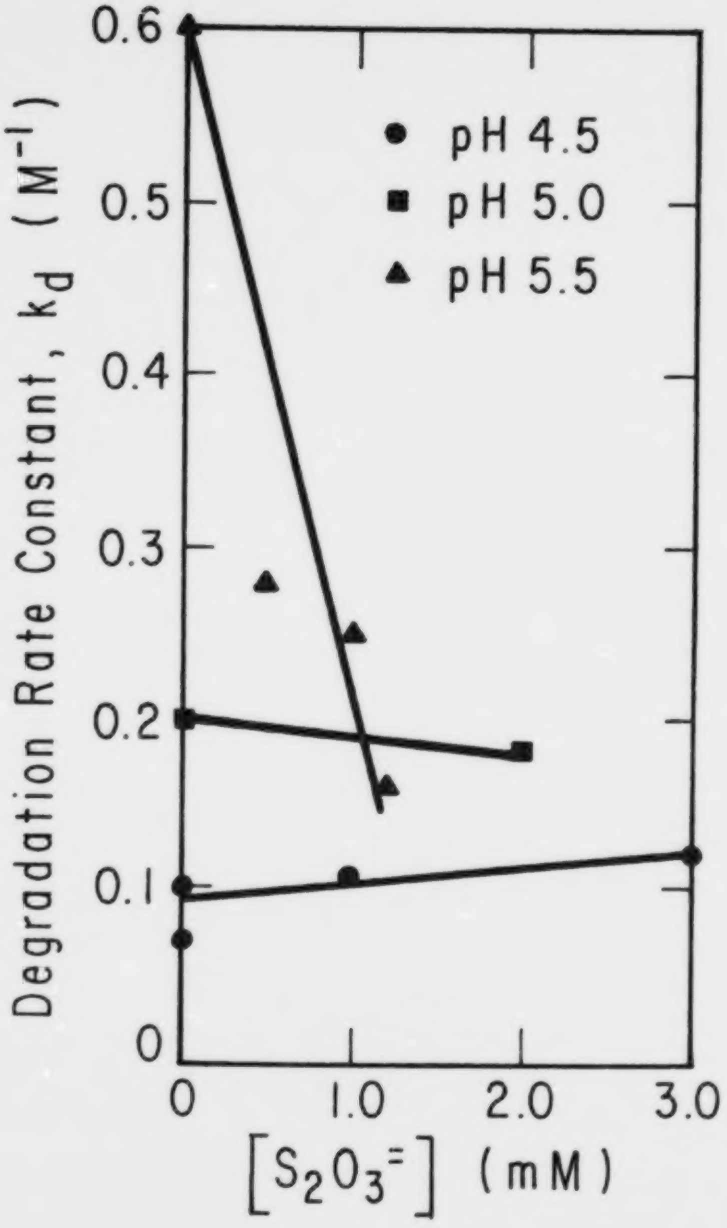


Figure 3-17. Effect of thiosulfate on adipic acid degradation, 1.0 mM Mn.

from 36 to 55%. These gaseous products could be carbon dioxide and straight chain hydrocarbons from methane to n-butane. There was a much higher fraction of degradation products identified in A19, the only run without Mn.

The GC chromatogram of A19 is shown in Figure 4-18. It was found that peaks 94 and 117 could contribute a significant fraction of the unidentified degradation products. Glutaric acid (peak 134) and succinic acid (peak 86) were smaller than either peak 94 or peak 117.

The mass spectrum of the major product, peak 94, is shown in Figure 4-19. Table 3-5 gives the relative abundance of each fragment formed. Isotope abundance ratio of major m/e is shown in Table 3-6 for both measured and calculated values. Figure 4-20 gives the mechanism of fragmentation of the methyl ester of 4-carboxy-butanal. The fragments fit nicely with the mass spectrum of peak 94. In addition, 4-carboxy-butanal seems to be a reasonable degradation product of adipic acid in the absence of Mn. Figure 4-21 shows the possible mechanism of degradation of adipic acid to 4-carboxy-butanal.

If we assume that 4-carboxy-butanal has the same sensitivity response on the GC as adipic acid, peak 94 contributes 0.06 gC/l.

A series of experiments were run to investigate the effect of Mn on degradation products. All of these experiments were run at pH 5.5 but with different amounts of Mn. Table 4-7 gives the degradation products of adipic acid.

Little valeric acid was formed in the absence of Mn. A small amount of valeric acid was detected in A21 with only 0.1 mM Mn, while much more valeric acid was detected in G3 without Mn, and only a trace amount of butyric acid was in G4 with 0.1 mM Mn.

Unknown 422, having a retention time of 422 seconds at the GC conditions described in the appendix, has an opposite trend. From the mass spectra of adipic acid and glutaric acid experiments, it seems that unknown 422 degraded from adipic acid is different from the unknown 422 degraded from glutaric acid, although they came out at the same retention time on the chromatogram.

For the nonvolatile degradation products, it was found that 4-carboxy-butanal and peak 117 were major degradation products of adipic acid with low Mn, while glutaric acid was the major degradation product with high Mn.

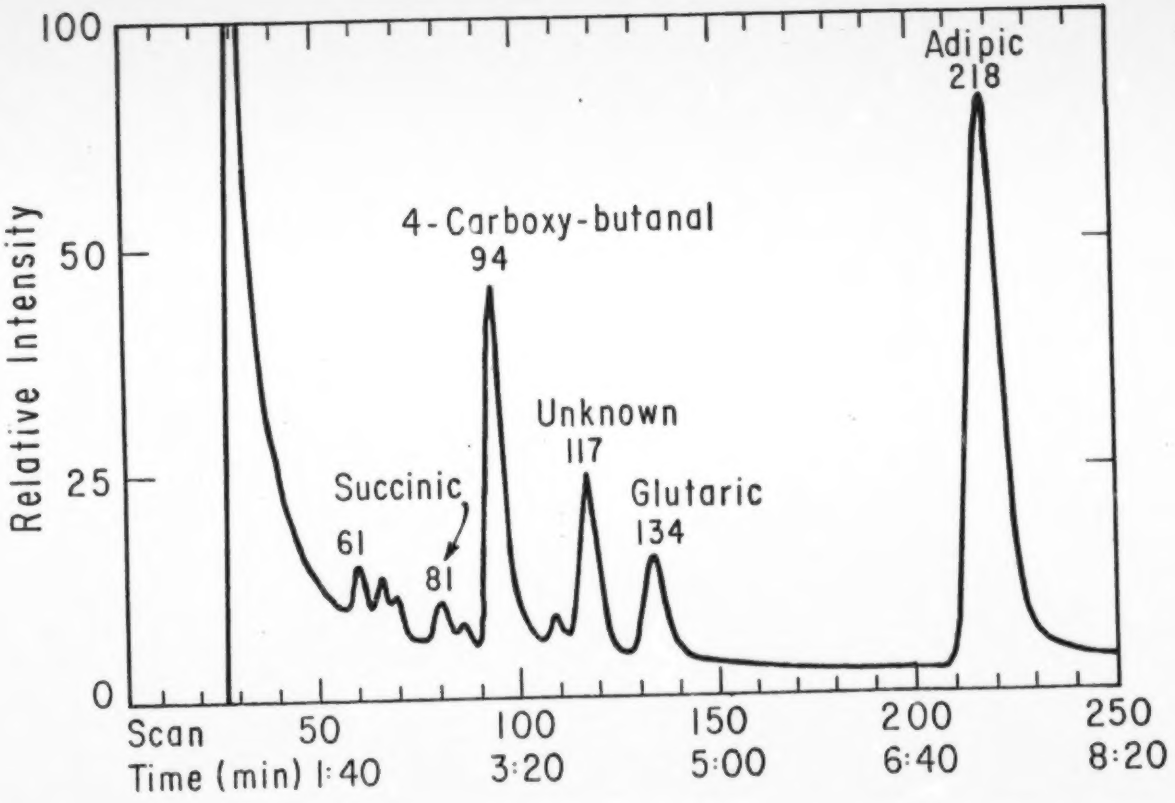


Figure 3-18. GC/MS Chromatogram of final sample from A19

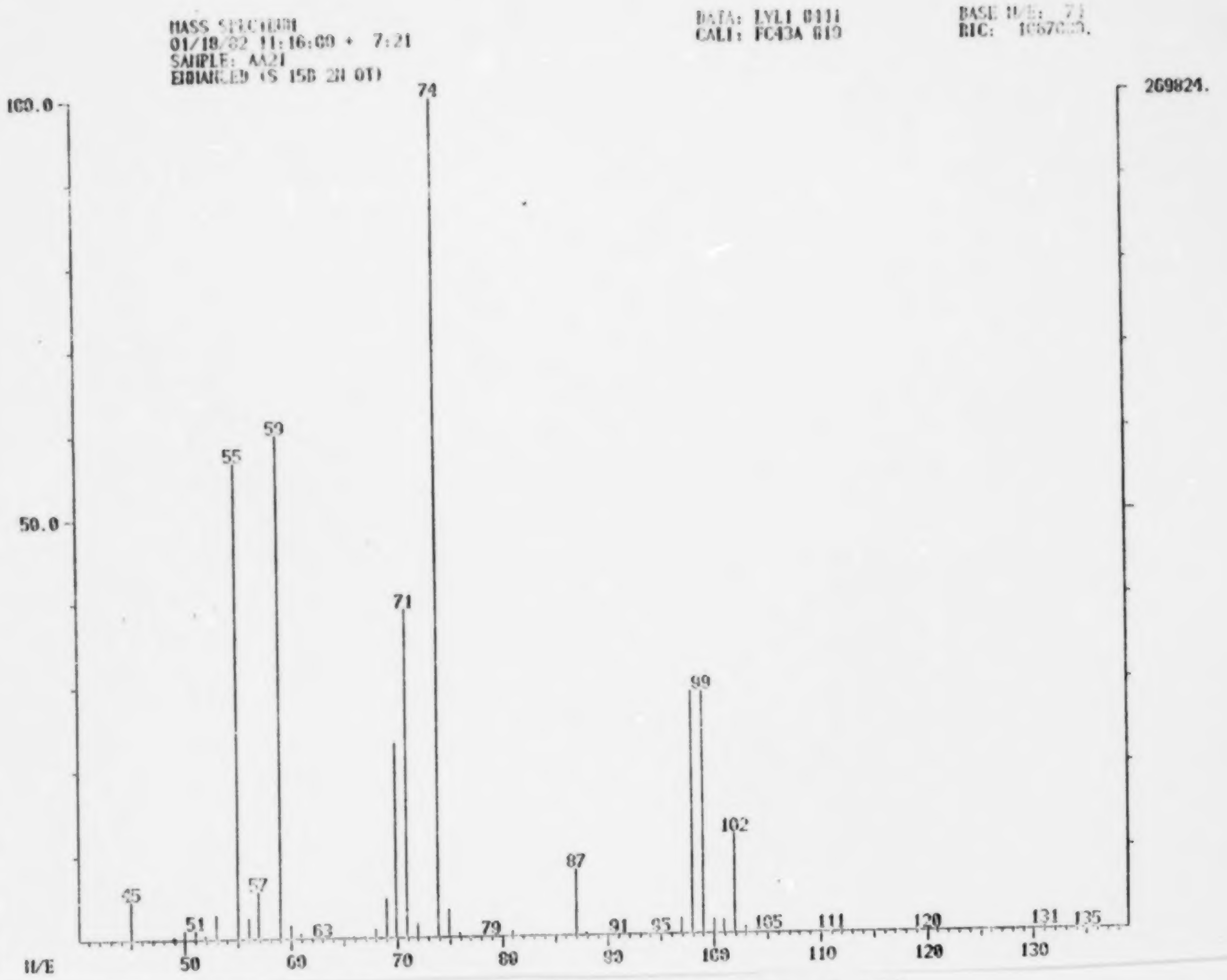
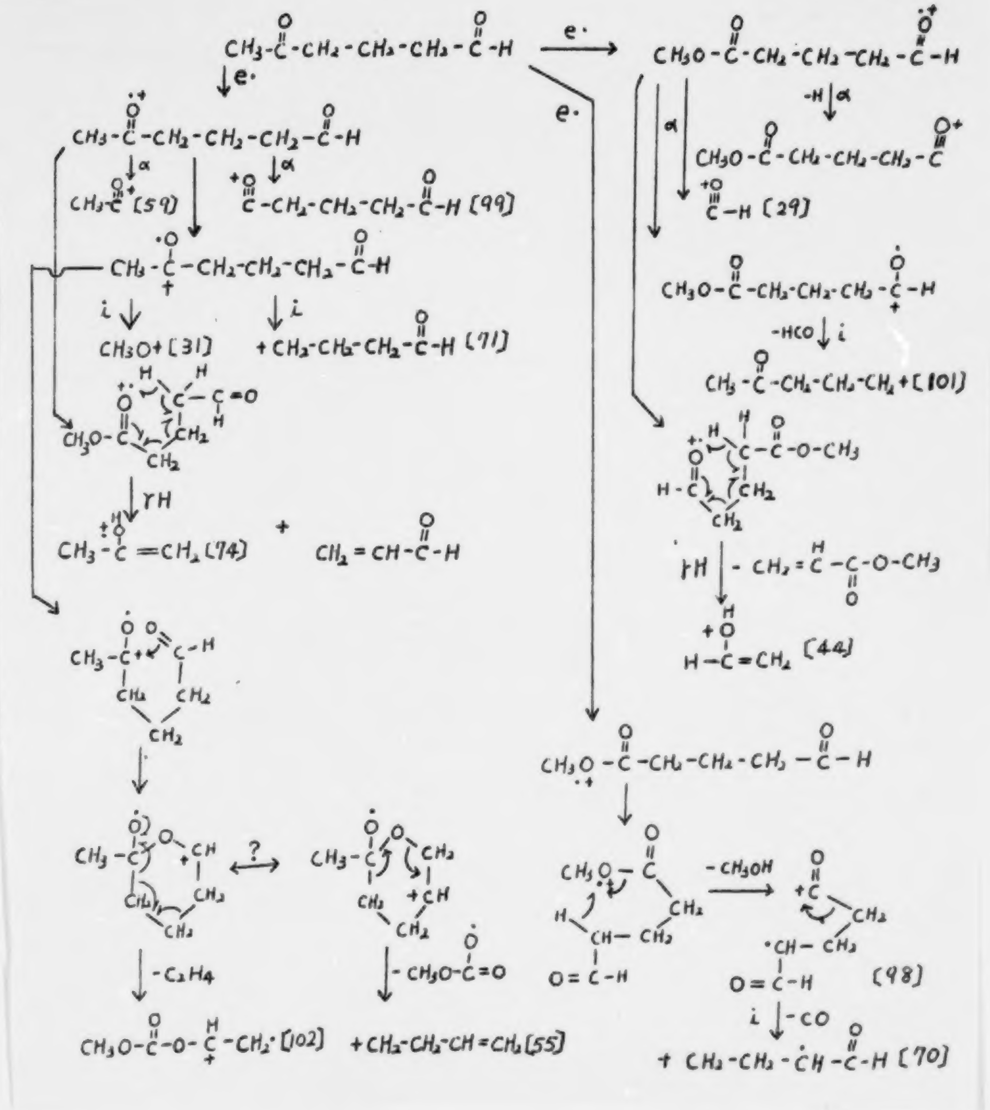


Figure 3-19. Mass Spectrum of Peak 94 of A19



e·
α
i
γH
[59]
[99]
[31]
[71]
[74]
[29]
[101]
[44]
[102]
[55]
[98]
[70]
-CH₃OH
-HCO
-C₂H₄
-CO
?

Figure 3-20. The mechanism of mass fragmentation of 4-carboxy-butanal

Table 3-5. Values of m/e for 4-Carboxy-butanal

```
MASS LIST                      DATA: LYL1 # 441         BASE M/E:   74
01/13/82 11:16:00 +  7:21      CALI: FC43A #  19        RIC:    1067000.
SAMPLE: AA21
CONDS.:
FORMULA:                       INSTRUMENT: FINN         WEIGHT:    0.000
SUBMITTED BY:                  ANALYST:                 ACCT. NO.:
ENHANCED (S 15B 2N 0T)

   45       0.00   0.00      0. MINIMA     MIN INTEN:      0.
  135                    # 400  MAXIMA
 MASS       % RA  % RIC  INTEN.     MASS        % RA  % RIC   INTEN.

  45.0      4.49   1.14  12128.    120.0        0.03   0.01      71.
  49.0      0.27   0.07    727.    121.0        0.02   0.00      44.
  50.0      0.99   0.25   2664.    122.0        0.01   0.00      31.
  51.0      1.01   0.26   2732.    130.0        0.01   0.00      14.
  52.0      0.44   0.11   1194.    131.0        0.33   0.08     900.
  53.0      2.80   0.71   7552.    135.0        0.01   0.00      15.
  55.0     56.64  14.32 152832.
  56.0      2.47   0.62   6656.
  57.0      5.47   1.38  14768.
  59.0     59.96  15.16 161792.
  60.0      1.49   0.38   4028.
  61.0      0.55   0.14   1480.
  63.0      0.01   0.00     15.
  65.0      0.06   0.01    156.
  66.0      0.12   0.03    318.
  67.0      0.15   0.04    398.
  68.0      0.95   0.24   2576.
  69.0      4.70   1.19  12672.
  70.0     23.10   5.84  62336.
  71.0     39.09   9.88 105472.
  72.0      1.77   0.45   4768.
  74.0    100.00  25.29 269824.
  75.0      3.30   0.83   8896.
  76.0      0.44   0.11   1192.
  77.0      0.06   0.02    162.
  78.0      0.02   0.00     52.
  79.0      0.05   0.01    132.
  80.0      0.03   0.01     78.
  81.0      0.58   0.15   1560.
  87.0      7.76   1.96  20928.
  88.0      0.31   0.08    827.
  89.0      0.04   0.01    107.
  91.0      0.07   0.02    177.
  92.0      0.01   0.00     30.
  95.0      0.05   0.01    130.
  97.0      1.83   0.46   4928.
  98.0     28.84   7.29  77824.
  99.0     28.89   7.31  77952.
 100.0      1.72   0.43   4632.
 101.0      1.56   0.40   4216.
 102.0     11.82   2.99  31904.
 103.0      0.64   0.16   1738.
 104.0      0.06   0.01    149.
 105.0      0.12   0.03    312.
 111.0      0.20   0.05    543.
 112.0      0.11   0.03    297.
 113.0      0.01   0.00     34.
```

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Table 3-6: Isotope abundance and formula of fragments of peak 94 in the GC/MS chromatogram of A19

P(m/e)	P + 1 (%) measured	P + 1 (%) calculated	P + 2 (%) measured	P + 2 (%) calculated	Formula
55	4.36	4.43	-	0.08	C_4H_7
59	2.48	2.29	0.92	0.42	$C_2H_3O_2$
71	4.53	4.47	-	0.28	C_4H_7O
74	3.30	3.42	0.44	0.44	$C_3H_6O_2$
87	3.99	4.51	0.52	0.48	$C_4H_7O_2$
98	-	5.58	-	0.53	$C_5H_6O_2$
99	5.74	5.59	-	0.53	$C_5H_7O_2$
102	5.41	4.54	0.51	0.68	$C_4H_6O_3$

Table 3-7: Organic Acids in Solutions of Adipic and Glutaric Acids Degraded at pH 5.0, Concentrations in mM

Run No.	AA21	AA23	AA24	G3	G4
Mn	0.1	3.0	0.1	0.0	0.1
Initial Adipic or Glutaric	10	10	50	10	10
Adipic	1.40	5.20	40.0	-	-
Glutaric	0.55	0.45	3.20	1.80	1.60
Unknown 117[a]	0.50	-	0.70	0.4	0.24
4-Carboxy-butanal	2.50	0.04	12.0	-	-
Succinic	0.20	0.04	2.40	0.03	0.30
Malonic	0.50	-	0.50	1.30	1.15
Valeric	0.09	0.50	0.50	-	-
Unknown 422[b]	0.40	0.03	1.35	0.80	0.50
Butyric	0.06	0.03	0.06	-	0.03

---

[a] Standardized assuming same area response as adipic acid

[b] Standardized assuming same area response as valeric acid

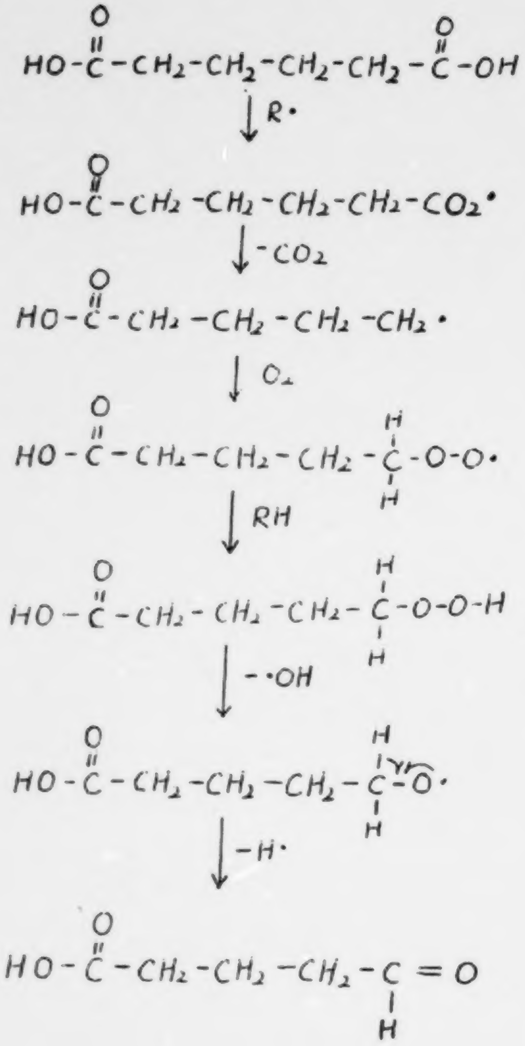
R·
-CO₂
O₂
RH
-·OH
-H·

Figure 3-21 The mechanism of formation of 4-carboxy-Butanal from the oxidative degradation of adipic acid.

DATA COMPARISON

One of the objectives of this work was to verify some of field testing results of adipic acid degradation. Generally, the degradation rate at pH 4.3-5.5 in this work is lower than that of RTP and Radian. Coprecipitation is important at RTP, Radian, and Shawnee but is not a problem in this work because only pure gypsum was precipitated.

Figure 4-22 shows the comparison between the degradation rate constant k_d obtained in this work and at Shawnee. Our k_d values without Mn and with 0.3-1.0 mM Mn estimate conservatively the Shawnee k_d values in natural oxidation and forced oxidation. Data from both sources showed that the degradation rate increases with increasing pH.

CONCLUSIONS

1. Adipic acid degradation can be reduced if operating at low pH (4.5) with $[Mn^{++}]$ 0.3 mM.

2. High concentration (10 mM) hydroxycarboxylic acids inhibit sulfite oxidation and the acids do not degrade. Low concentrations of hydrocarboxylic acids degrade at a slower rate than adipic acid.

3. Thiosulfate inhibits sulfite oxidation and partially inhibits adipic acid degradation.

4. As much as 40% of the degradation products of adipic acid are volatile CO_2 and hydrocarbons.

5. In the presence of 1.0 mM Mn^{++}, the retained degradation products are primarily valeric and glutaric acids. With a low concentration of Mn^{++} (0.1 mM), the degradation products are significantly different and include significant quantities of 4-carboxy-butanal.

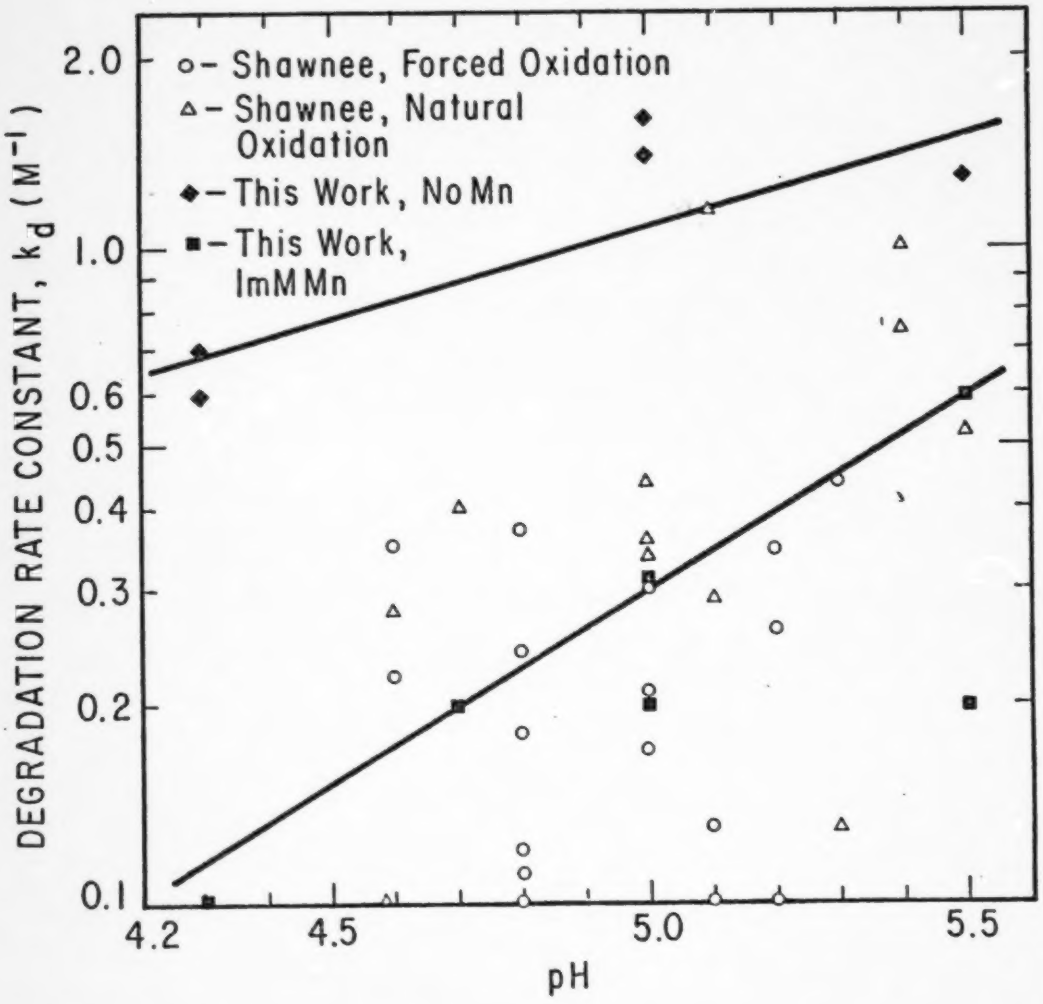

Figure 3-22. Degradation Rate Constant as a Function of pH at the University of Texas and Shawnee Prototype Plant

APPENDIX 3-A

CALCULATION FOR ADIPIC ACID LOSSES

Table 3-8: RTP Field Testing Data

	Forced Oxidation	Natural Oxidation
% Degradation	64	39
Adipic Acid Con., g/hr	0.633	1.63
Adipic Acid Feed, g/hr	17.2	26.8
Wet Filter Cake Recovered, lb/hr	20.2	28.0
Filter Cake Solids, %	86	50.0
Liquor Loss in Filter Cake, l/hr	1.3	6.7
SO_2 Feed Rate, lb/hr	6.25	6.4
SO_2 Absorption, %	87.8	94

CALCULATION

Basis: 1 hour operation

$$\text{Mole } SO_2 \text{ absorbed} = SO_2 \text{ feed rate x \% } SO_2 \text{ absorption x } \frac{\text{1 lb mole}}{\text{64 lb } SO_2} \text{ x } \frac{\text{453.6 gmole}}{\text{1 lbmole}}$$

$$\text{Loss in liquor solution} = \frac{\left[\text{ liquor loss in filter cake x adipic acid conc. x } \frac{\text{1 mole adipic acid}}{\text{146 g adipic acid}}\right]}{\text{mole } SO_2 \text{ absorbed}}$$

$$\text{Degradation loss} = \frac{\left[\text{ adipic acid feed x \% degradation x } \frac{\text{1 gmole adipic acid}}{\text{146 g adipic acid}}\right]}{\text{mole } SO_2 \text{ absorbed}}$$

Loss in coprecipitation

forced oxidation = 0

natural oxidation = 500 ppm

$$\text{loss} = \frac{\left[\text{ wet filter cake recovered x \% filter solids x } \frac{\text{454 g solids}}{\text{lb solids}} \text{ x } \frac{\text{500 g adipic acid}}{10^6 \text{ g solids}}\right]}{\text{mole } SO_2 \text{ absorbed}}$$

APPENDIX 3-B
RESULTS OF ADIPIC ACID TESTING AT RTP, SHAWNEE, AND RADIAN

Table 3-9: Summary of RTP Work[a]

Progress Report No.	Date	pH	k_d^b (M^{-1})	% Oxidation	Comments
28	Oct. 30-Nov. 3	6.2	0.5	20	-
28	Oct. 16-20	6.1	0.9	15	-
38	Nov. 6-10	6.1	0.5	83	-
38	Nov. 13-17	6.1	0.4	97	-
38	Nov. 27-Dec. 1	6.1	0.5	99	-
28	Oct. 23-27	5.5	0.4	17	-
47	Aug. 18-29	5.7	0.3	22	0.34 mM Mn
42	Mar. 17-21	4.6	0.2	29	-
42	Mar. 24-28	4.6	0.2	35	-
42	Mar. 31-April 4	4.6	0.2	26	-
43	April 14-17	4.6	0.2	22	-
45	June 16-20	4.6	0.4	25	-
45	June 23-27	4.6	0.4	29	-
43	April 28-May 1	4.6	0.3	22	55 g/hr $FeCl_2$
43	May 5-8	4.6	0.3	25	55 g/hr $FeCl_2$
47	Sept. 2-12	4.6	0.2	32	1.0 mM Mn
46	July 28-Aug. 1	4.6	0.05	55	0.34 mM Mn
47	Sept. 15-26	4.5	0.5	20	0.6 mM Mn 0.22 mM Fe
45	June 2-13	4.6	0.4	27	30% flyash

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[a] Borgwardt, R. H., EPA-IERI Progress Reports, 1977-1980

[b] Calculation based on total adipic acid loss through degradation and coprecipitationx

CALCULATION OF k_d

$$k_d = \frac{\text{(adipic acid fed per hour, mole/hr) (\% degradation)}}{(SO_3^= \text{ oxidized per hour, mole/hr) (adipic acid concentration, M)}}$$

Sample Calculation for P.R. #28, Oct. 16-20:

adipic acid fed = 28.6 g/hr x mole/146 g = 0.20 mole/hr

adipic acid fed = (28.6 g/hr) x (mole/146 g) = 0.20 mole/hr

$SO_3^=$ oxidized per hr = (SO_2 fed per hour, lb/hr) x (% SO_2 absorbed) x
(% oxidation) x (mole SO_2/64 g SO_2) x
(1 mole $SO_3^=$/1 mole SO_2) x (454 g/lb)
= (6.4 x 0.94 x 0.15 x 454)/64
= 6.40 mole/hr

adipic acid concentration = (2.05 g/l) x (mole adipic acid/146 g)
= 0.014 M

k = (0.2 x 0.4)/(6.40 x 0.014) = 0.9 M^{-1}

Table 3-10: Summary of Shawnee Work

Date	Run No.	pH	k_d[b] (M^{-1})	% Oxidation	$[Mn]_{mM}$
Venturi/Spray Tower, Limestone, Single Tank[a]					
12/18/79	926-1A	4.6	-	49	0.14
1/3/80	926-1G	4.9	0	51	-
1/16/80	926-1B	4.9	0	49	-
1/24/80	926-1C	5.1	0.04	47	-
1/29/80	926-1H	5.3	0.13	30	0.16
2/8/80	926-1D	5.5	0.53	17	0.14
2/15/80	926-1E	5.1	0	32	-
Venturi/Spray, Limestone, One Tank[a]					
3/13/80	914-1A	4.6	0.35	99	-
4/7/80	914-1C	4.7	0.4	32	-
Venturi, Limestone, One Tank[a]					
3/21/80	927-1M	5.1	0.13	99	-
4/7/80	914-1C	4.7	0.4	32	-
Venturi, Limestone, One Tank[a]					
3/21/80	927-1M	5.1	0.13	99	-
3/26/80	927-1N	5.2	0.26	99	-
3/30/80	927-1O	4.6	0.22	99	-
4/2/80	927-1P	5.1	1.23	23	-
Venturi/Spray, Limestone[a]					
4/24/80	916-1A	4.8	0.18	100	-
4/28/80	916-1B	4.8	0.04	100	-
5/2/80	916-1C	4.9	-	100	-
5/6/80	916-1D	5.1	-	100	-
5/13/80	916-1E	5.1	0.13	100	-
5/19/80	916-1F	5.1	0.09	100	-
5/22/80	916-1G	5.3	0.44	100	-

Table 3-10 (continued)

Date	Run No.	pH	k_d[b] (M^{-1})	% Oxidation	[Mn] mM
(Venturi/Spray, Limestone[a])					
5/24/80	916-1H	5.1	0.13	50	-
-	917-1A	5.0	0.17	100	(high conc. M^{++})
TCA, Limestone, Natural Oxidation[c]					
7/18/80	934-2C	5.4	1.0	42	-
7/31/80	934-2A	4.6	0.06	57	-
8/5/80	934-2B	5.0	0.34	40	-
8/9/80	934-2E	5.0	0.44	38	0.06
8/14/80	934-2F	4.6	0.28	50	0.1
8/20/80	934-2D	5.4	0.75	23	0.04
8/27/80	934-2G	5.0	0.36	27	-
9/2/80	934-2H	5.1	0.29	25	0.06
TCA, Limestone, Forced Oxidation[c]					
9/11/80	907-2A	4.8	0.37	100	-
9/22/80	907-2B	4.8	0.12	98	0.56
9/25/80	907-2C	4.8	0.24	99	-
10/4/80	907-2D	4.8	0.11	100	-
10/10/80	907-2E	4.8	0.01	100	0.92
10/16/80	907-2F	4.8	0.07	100	0.98
10/21/80	907-2G	4.8	0.10	100	0.22
10/27/80	907-2J	5.0	0.30	100	0.82
11/3/80	907-2K	5.0	0.21	100	0.84
11/7/80	907-2L	5.2	0.35	100	0.92
11/31/80	907-2M	5.2	0.08	91	0.106

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[a] Burbank et al., 1980

[b] Calculation based on total adipic acid loss through degradation and coprecipitation

[c] Bechtel, 1980

CALCULATION OF k_d

$$k = \frac{\text{mole of adipic acid loss}}{(\text{mole of } SO_2 \text{ abs.})\ (\%\ \text{oxidation})\ (\text{adipic acid conc., M})}$$

Theoretical adipic acid = actual adipic acid x (theor./actual) x (1b adipic/2000 1b SO_2 abs.)

Adipic acid loss = actual adipic acid - theor. adipic acid

Adipic acid conc. = (ppm adipic acid/1000 x 146)(M)

Sample Calculation for Run 926-H:

theor. adipic acid = 8.0/1.24 = 6.45

adipic acid loss = 8.0 - 6.45 = 1.55 1b/2000 1b SO_2 abs.
= 0.011 1bmole/2000 1b SO_2 abs.

adipic acid conc. = (1285/1000 x 146) = 0.0088 M

mole SO_2 abs. = (2000 1b/64 1b/mole) = 31.25 mole

k_d = (0.011/31.25 x 0.3 x 0.0088) = 0.13 M^{-1}

Table 3-11: Summary of Radian Work

Date	Run #	pH	% Oxidation	k_d[b] (M^{-1})
Laboratory Batch Reactor				
-	2[a]	6.0	-	2.7
-	3	6.0	-	1.8
-	4	4.5	-	0.9
-	5	4.5	-	0.4
Laboratory Bench-Scale Study				
5/29/80	4[c]	4.6	41	0.2[d]
5/22/80	3A	4.6	63	0.1[d]
7/1/80	5	4.6	99	1.4
7/7/80	C	4.6	99	0.7
7/8/80	10	4.6	99	0.9
5/21/80	2	5.5	27	0.9[d]
7/11/80	A	5.5	81	0.6
7/9/80	7	5.5	99	0.7
2/2/81	R9	4.6	12	1.0
2/4/81	R10	5.1	10	1.2
2/9/81	R11	5.5	11	0.5
2/10/81	R12	5.1	11	1.0
2/11/81	R13	4.6	100	1.3
2/12/81	R14	5.1	100	0.24
-	R15	4.6	42	1.28
-	R16	5.1	11	1.63 (0.02-0.04 mM Mn)
-	R17	4.6	100	0.52 (94°F)
-	R18	5.1	100	1.78
-	R19	5.1	100	1.78
-	R20	5.5	61	2.03
-	R21	5.5	23	0.98 (2000-3500 ppm $SO_3^=$)
-	R22	5.1	20	1.15

Table 3-11 (continued)

Date	Run #	pH	% Oxidation	k_d[b] (M^{-1})
Shawnee Bench-Scale Study[c]				
8/6/80	S-1	4.6	19	0.9[d] (0.002 mM Mn)
8/7/80	S-2	4.6	18	1.4 (0.002 mM Mn)
8/8/80	S-3	4.6	12	2.0 (0.006 mM Mn)
Springfield Bench Scale Study[c]				
8/21/80	P1	4.6	12	1.2 (0.03 mM Mn)
9/6/80	P4	4.6	11	1.2[d] (0.032 mM Mn)
9/5/80	P3	4.6	22	0.4[d] (0.24 mM Mn)
8/23/80	P2	4.6	7	2.4 (0.15 mM Mn)

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[a] Meserole et al., 1980

[b] Calculation based on total adipic acid loss through degradation and coprecipiation.

[c] Terry et al., 1981

[d] Large deviation associated with experimental data.

CALCULATION OF k_d

Glass Batch Reactor

k_d = $(\ln[A]_2/[A]_1)/([SO_3^=]_2 - [SO_3^=]_1$

[A] , [A] = Initial and final adipic conc., mM.

$[SO_3^=]_1$, $[SO_3^=]_2$ = Initial and final adipic conc., mole.

Sample Calculation: Run 2

$k_d = (\ln 11.3/13.7)/(0.27-0.341) = 2.7\ M^{-1}$

Bench Scale Scrubber

k = (mg adipic degraded/g SO_2 removed) x

(mole adipic/1.46x10^5 mg adipic) x (64 g SO_2/mole SO_2) x

(1.46x10^5 ppm adipic/ppm adipic x 1 mole adipic) x (1/% oxidation)

Sample Calculation: R1

$k_d = (9.4 \times 64 \times 1.46 \times 10^5)/1.46 \times 10^5 \times 0.27 \times 2366)$

$= 0.94\ M^{-1}$

APPENDIX 3-C

IODINE TITRATION

PREPARATION OF pH 6 BUFFER SOLUTION

This solution contains 1 mole/l NaAc and 0.05 mole/l HAc. Pipet 2.9 ml of glacial acetic acid into 500 ml of D.I. water. Stir in 82 grams of NaAc and after completely dissolved make up to one liter.

PROCEDURES FOR IODINE TITRATION

1. Pipette one milliliter of slurry into an agitated beaker.
2. Add approximately 30 ml of pH 6 acetate buffer solution to the slurry.
3. Pipette 2 ml of 1 N iodine and add few drops of starch indicator. Stir the solution until all slurry solids have dissolved. Decrease the amount of 1 N iodine for samples containing low sulfite concentration.
4. Back titrate the excess iodine with 0.1 M sodium thiosulfate until the color of the solution turns clear.
5. Record the volume of 0.1 M sodium thiosulfate used.

CALCULATION OF TOTAL SULFITE CONCENTRATION

The concentration (mole/liter) of sulfite present in the slurry solution can be determined by use of the following equation:

$$C = \frac{2(B-S)M}{V}$$

C = Concentration of sulfite, mole/l

B = Volume of sodium thiosulfate used to titrate the blank, ml

S = Volume of sodium thiosulfate used to titrate the sample, ml

M = Concentration of the sodium thiosulfate, moles/l

V = Volume of sample, ml

APPENDIX 3-D

ION CHROMATOGRAPHY

THEORY

Ion chromatography (IC) is an easy and fast analytical method used to identify and quantitate organic and inorganic species in solution. IC combines the efficient separation capability of ion exchange resins with conductimetric detection. The ionic species are separated according to the differences of their affinity for the ion exchange resins, and they are identified by their elution times. The measured conductance of each ionic species is linearly proportional to its concentration. The separating power of the IC is a function of the type of eluent and its flow rate. A combination of sodium carbonate and sodium bicarbonate is the most commonly used eluent. The analysis requires only less than one milliliter of the sample solution, and the detection limit is 50 parts per billion or less.

Ion exchange resins used in IC are composed of a spherical polystyrene matrix crosslinked with divinylbenzene. Functional groups such as sulfonic acid of quaternary ammonium are then chemically bonded in the matrix. These groups provide exchange sites where their counter ions are exchanged with sample ions as the sample flows through the resin bed. Ion exchange reactions are reversible and proceed stoichiometrically.

In order to combine conductivity detection with ion exchange separation, a method was required for removing the background ions in the effluent stream. This is accomplished by placing a second special ion exchange column downstream from the separator column. The resins in the second column are capable of suppressing the conductivity of the eluent while converting the ions of the sample to a common ionic form. If a series of anions is to be separated using $NaHCO_3$ as the eluent, a strong base anion exchanger in the HCO_3^- form is used in the separator column and a strong acid cation exchanger in the H^+ form is used in the suppressor column. The suppressor reactions are:

(1) $NaHCO_3 + \text{Resin-H} \rightleftarrows \text{Resin-Na} + H_2CO_3$

(H_2CO_3 has very low conductance)

(2) $Na^+X^- + \text{Resin-H} \rightleftarrows \text{Resin-Na} + H^+X^-$

X^- represents the anion to be separated.

SAMPLE SOLUTION PREPARATION

Vacuum filter the slurry samples. The analytical concentration of adipic acid is between 0.1 mM and 0.2 mM. Dilute the filtered samples to within the analytical concentration with distilled water, then dilute again with a double strength eluent to give a final sample solution with an equal eluent concentration. Dilution with a double strength eluent will eliminate the occurance of a negative water peak.

ADIPIC ACID STANDARD PREPARTION

Weigh out 1.462 grams of adipic acid on a mettler balance (accuracy ±0.001) and pour into a one-liter volumetric flask. Dissolve adipic acid in distilled water and make the total volume to 1 liter. This gives a 10 mM adipic acid stock solution. Prepare a number of adipic acid standards within the concentration range of 0.01 mM to 0.12 mM from the 10 mM adipic acid stock solution by dilution with distilled water and then with the double strength eluent.

ANALYTICAL CONDITIONS

Table 3-12 gives the elution time of various chemical species using different eluents. Elution time increases with decreasing concentration and flow rate of the eluent. An example of adipic acid calibration curve is shown in Figure 3-23. Height of adipic acid in inches was converted to conductance using the calibration constant of the system, 10^{-4}. A sample chromatogram for run A15, t = 0 is given in Figure 3-24.

Table 3-12: IC System Conditions and Elution Time

Analytical Conditions[a]	Elution Time (Minutes) Adipate	Sulfate	Chloride
Eluent: 1.6 mM Na_2CO_3/2.0 mM $NaHCO_3$ Flow rate: 138 ml/min	~ 3.7	~ 5.8	~ 2.5
Eluent: 2.4 mM Na_2CO_3/3.0 mM $NaHCO_3$ Flow Rate: 138 ml/min	~ 10	~ 19	~ 4.0

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[a] 3 x 500 mm separator column
6 x 250 mm suppressor column

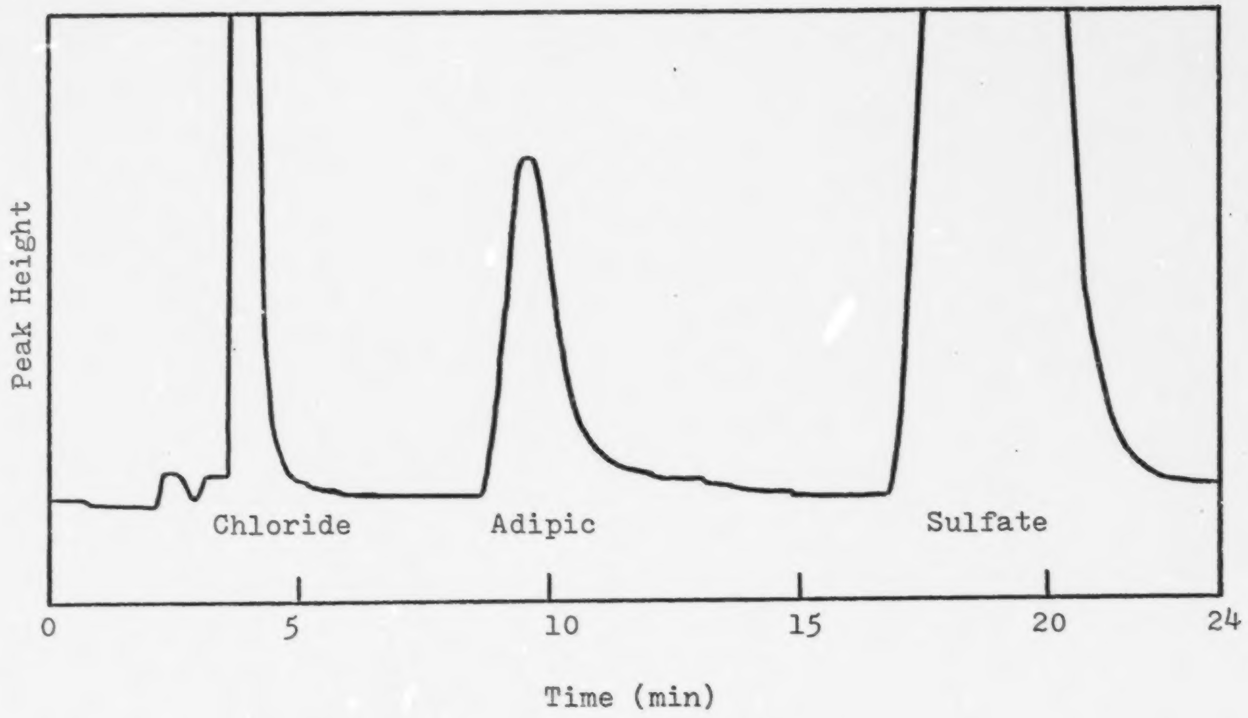


Figure 3-23. IC Chromatogram for Run A15 at t=0

2.4 mM Na_2CO_3/3.0 mM $NaHCO_3$ Eluent

138 ml/min Flow Rate

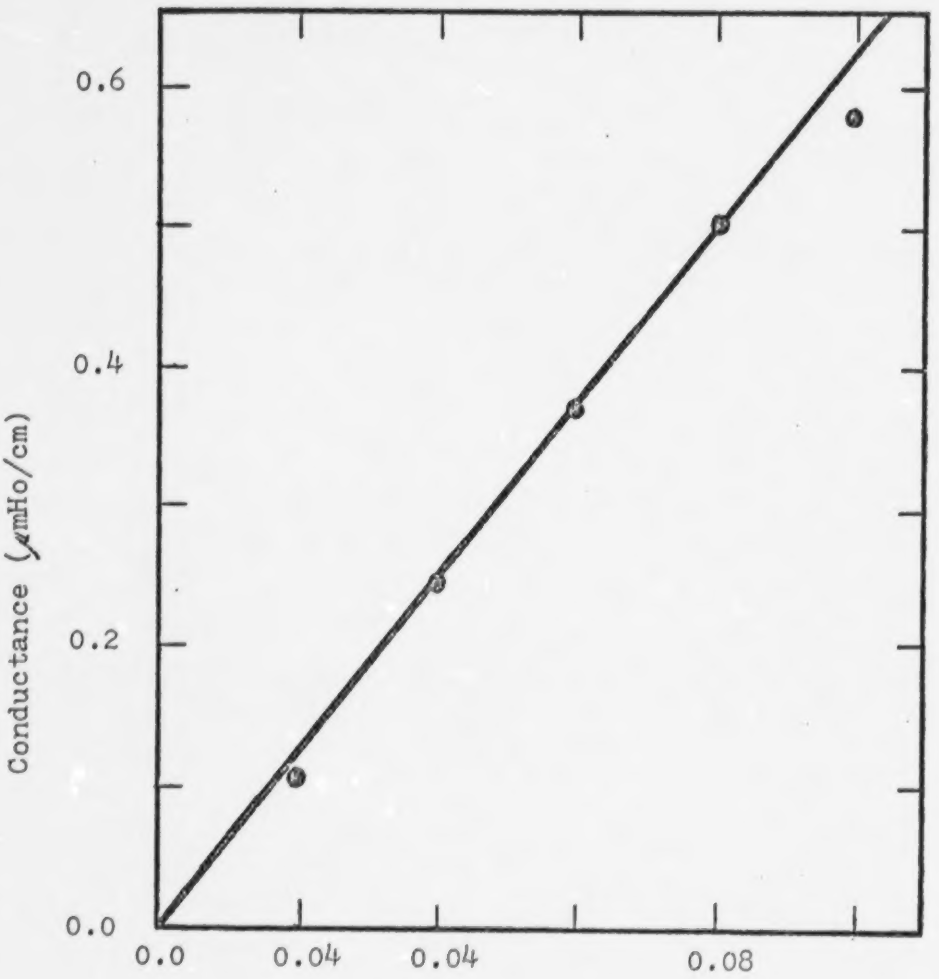


Figure 3-24. Sample IC Adipic Acid Standard Calibration Curve

APPENDIX 3-E

ION CHROMATOGRAPHY EXCLUSION

THEORY

Ion Chromatography Exclusion is a natural complement to IC due to its unique ability to separate inorganic and their salts from weaker organic acids. The system combines the efficient separation capabilities of ion exchange resins with conductive detection. Analysis requires only less than one milliliter of the sample solution, and the detection limit is well below 1 ppm. ICE has an additional advantage over IC in that it has a low conductance background. The commonly used eluent is dilute hydrochloric acid and it can be easily stripped from the eluent using a Ag^+ form suppressor:

$$H^+ + Cl^- + |{\sim}SO_3^-Ag^+ \rightarrow AgCl\downarrow + |{\sim}SO_3H^+$$

Accumulation of silver chloride precipitate demands periodic change of the suppressor column.

In ICE, the functional groups of the resins tend to form a semipermeable membrane between the eluent and the occluded liquid inside the resin pores. The presence of this membrane leads to the phenomenon known as Donnan Exclusion. Because of the high ionic concentration within the particles, a highly ionized species such as H_2SO_4 cannot penetrate the membrane and, thus, no retention occurs. A non-electrolyte can penetrate the pores. Thus, when passed through a column of ionic exchange resin, the ionic material travels at a faster rate than the nonionic material, and this results in a separation of the chemical species.

Concentrations of the organic acids are linearly proportional to their measured conductances. The major factors affecting the separation of weak organic acids include the following:

(1) Solute pK_a - the larger the pK, the larger the retention of a weak electrolyte.

(2) Concentration of solute - especially important for weak electrolyte

since ionization is a function of concentration.

(3) Eluent pH - the lower the pH, the longer the retention of a weak electrolyte since the proportion of the acid in the non-ionized form increases.

(4) Flow rate - since separation is diffusion dependent, slow flow rates are desirable.

SOLUTION PREPARATION

The slurry samples are filtered and diluted with distilled water. The final adipic acid concentration is 0.1 mM adipic acid in the time zero sample.

1.462 grams of adipic acid is dissolved in one liter of distilled water. This gives a 10 mM adipic acid solution. Adipic acid standards of the concentration 0.01 mM to 0.12 mM are prepared from the 10 mM adipic acid solution by dilution with distilled water.

ANALYTICAL CONDITIONS

Table 3-13 gives the elution time of various chemical species. Elution time decreases with decreasing eluent concentration and flow rate. ICE cannot separate propionic acid from adipic acid. The height of adipic acid peak is converted to conductance using the system calibration constant, 10^{-4}. A sample of adipic acid calibration curve is given in Figure 3-25.

Table 3-13: ICE Analytical Conditions and Elution Time

	Elution Time (Minutes)						
Analytical Conditions	Adipate	Glutaric	Succinic	Valeric	Propionic	Butyric	Sulfate
0.1 mM HCl eluent 46 ml/hr flow rate	22.4	18.2	14.8	30	-	-	8.0
0.1 mM HCl eluent 62.6 ml/hr flow rate	15.0	12.2	9.8	-	15.0	17.8	5.3
0.02 mM HCl eluent 62.6 ml/hr flow rate	11.0	8.7	-	-	-	-	5.3

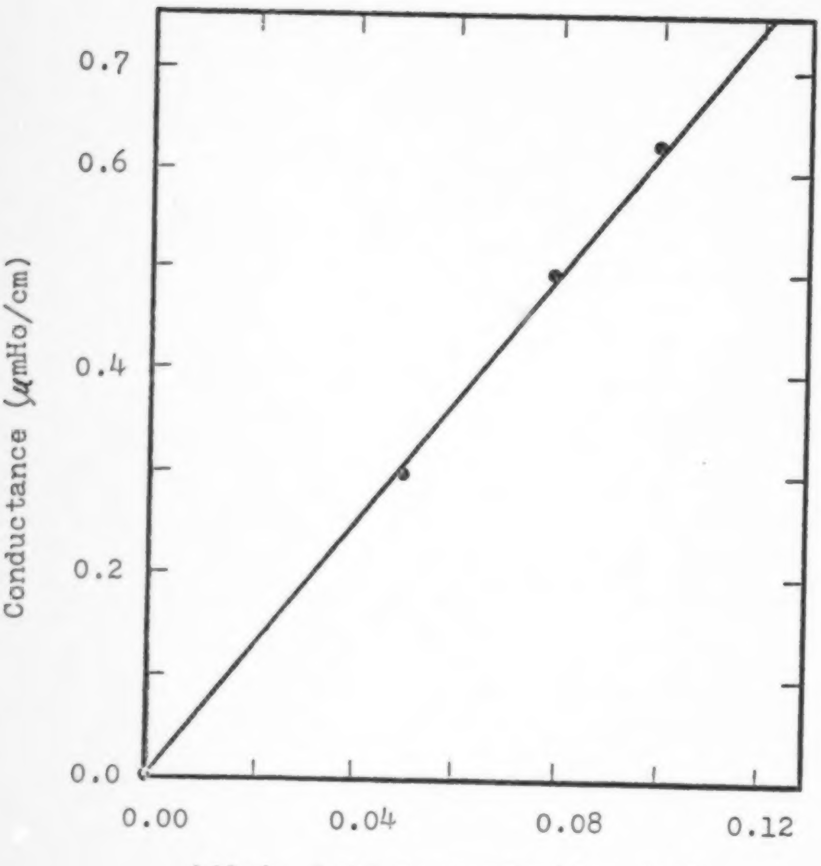


Figure 3-25. Sample ICE Adipic Acid Standard Calibration Curve

APPENDIX 3-F

ATOMIC ABSORPTION SPECTROPHOTOMETRY

THEORY

In atomic absorption photometry, a solution of a metallic salt is atomized into a high temperature flame. The solvent is evaporated, the salt is vaporized and the molecules are dissociated into neutral atoms. A discharge tube or lamp in which the cylindrical cathode is made of the element under investigation contains argon or helium carrier gas, at low pressure (1-2 mm). Application of a potential of several hundred volts across the electrode causes the cathod to emit radiation characteristic of the cathode material. When this beam of energy is passed through the vaporized sample interposed between the source and the entrance slit of a monochromator, set at a wavelength to isolate the spectral line of interest, the atomic vapors of the sample absorb this energy and thus decrease the radiant power of the beam. The radiant power of the spectral line is measured with a photomultiplier tube and amplifier, first without and then with the sample vapor in the optical beam; the decrease in radiant power is proportional to the number of atoms of the element under investigation in the beam. The method is calibrated with known amounts of the desired constituent, and a calibration curve is constructed from the data (Ayres, 1958).

APPENDIX 3-G

GAS CHROMATOGRAPHY

Two procedures were used for gas chromatography. Volatile acids were determined by extraction of acidified solutions with chloroform followed by injection of the chloroform phase. One ml chloroform and 0.1 ml 50% H_2SO_4 were added to 2 ml of aqueous sample. After shaking the mixture set for 15 minutes, one microliter of the chloroform phase was injected into the gas chromatograph. Table 3-14 and Figure 3-26 give the elution times and relative response for volatile acids. There was limited response for formic and acetic acids, probably because of poor extraction efficiency and reduced carbon number.

Nonvolatile acids were methylated in aqueous solution before extraction. Two ml of methanol and 0.5 ml of 50% H_2SO_4 were mixed with 1.0 ml sample and left overnight. Chloroform (0.5 ml) was mixed with the sample. After sitting for 15 minutes, 1 microliter of the chloroform phase was injected into the gas chromatograph. Table 3-15 and Figure 3-27 give the performance of the GC with this procedure.

Table 3-14: Summary of Retention Time and Response for Gas Chromatography of Monocarboxylic Acids

Acid	Retention Time (sec)	Relative Area Response
propionic	290	0.08
isobutyric	319	0.45
n-butyric	389	0.44
isovaleric	428	0.92
n-valeric	491	1.00
isocaproic	543	1.36
n-caproic	577	1.44
heptanoic	672	1.62

GC Conditions:

Column: Sp-1000
Injection: 170°C
FID: 180°C
Column: 110°C for 4 min, 10°C/min, 160°C for 5 min.
Sensitivity: 16×10^{-11}

Table 3-15: Retention Time and Response for Gas Chromatography of Esters of Dicarboxylic Acids

Acid	Retention Time (sec)	Relative Area Response
malonic	333	0.18
succinic	371	0.42
glutaric	419	0.71
adipic	483	1.00

GC Conditions:

Column: Sp-1000
Injection: 180°C
FID: 180°C
Column: 82°C for 2 min, 20°C/min, 160°C for 5 min.
Sensitivity: 32×10^{-11}

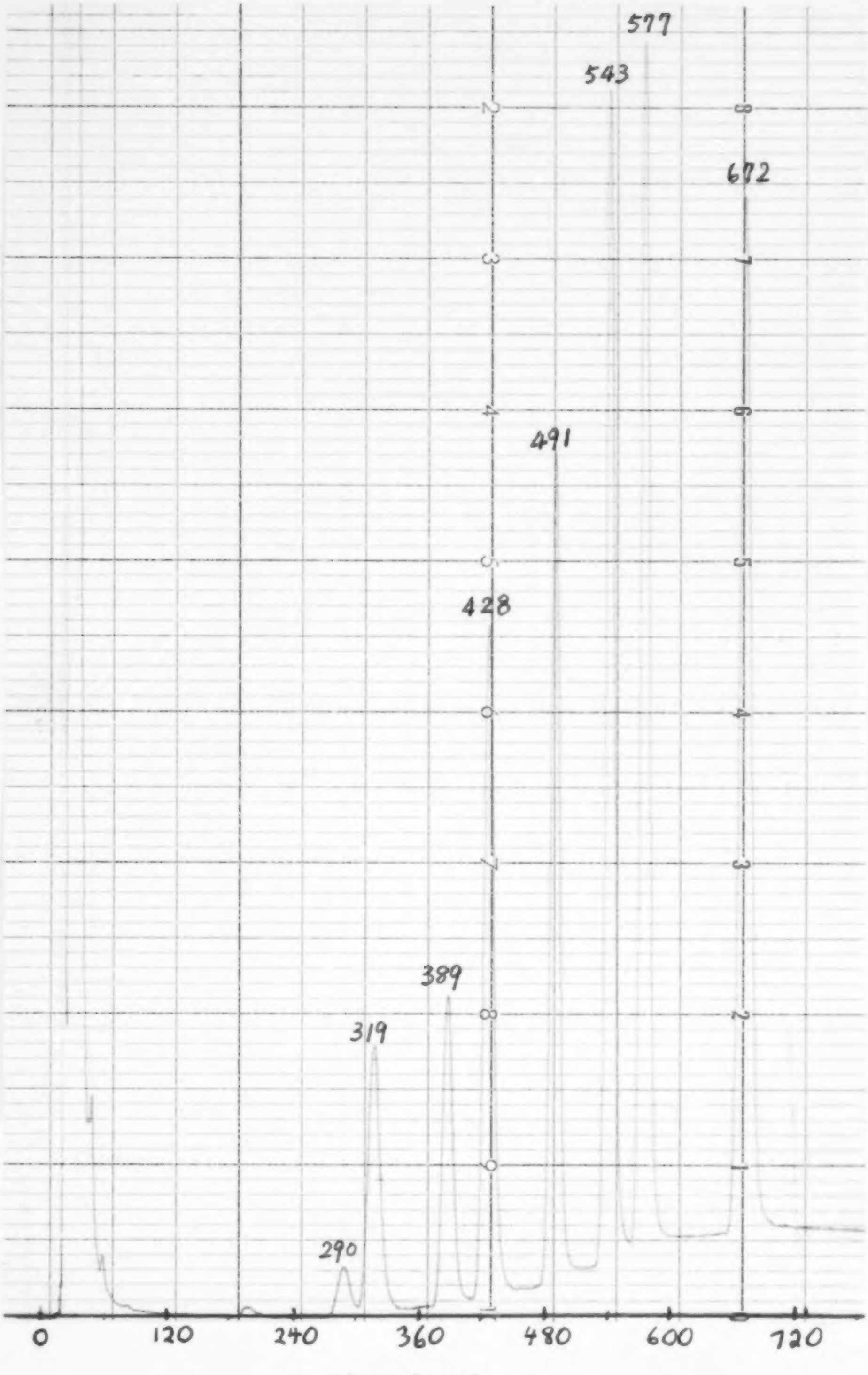
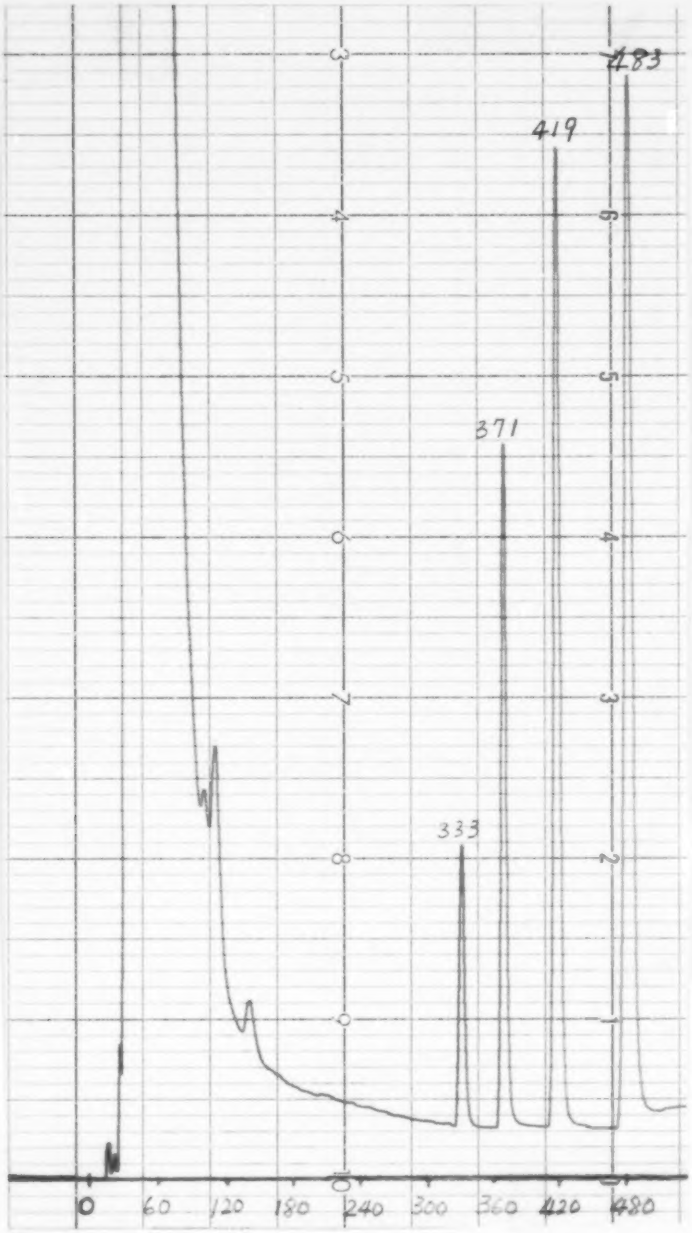


Figure 3-26. Chromatogram for monocarboxylic acids



TIME (SEC)

Figure 3-27. Chromatogram for Nonvolatile Acids

APPENDIX 3-H

TABULATED EXPERIMENTAL DATA

Table 3-16: Experimental Data Collected by W. Hsiang

Run No.	Time	pH	T(°C)	[$SO_3^=$] (M)	Adipic (mM)	% Degradation
Glass Batch Reactor						
A4	0 hr	4.3	-	0.93	9.4	0
	2 hr	4.2	-	0.87	7.9	16
	4 hr	4.2	-	0.82	7.1	24
	7 hr	4.3	-	0.79	6.0	36
	10 hr	4.3	-	0.67	-	-
	22 hr	4.5	-	0.25	6.1	36
	27 hr	2.7	-	0.06	3.9	59
A5	0 hr	5.0	-	0.95	9.7	0
	2 hr	4.85	-	0.85	9.0	7
	4 hr	4.83	-	0.77	7.5	24
	7.5 hr	5.20	-	0.72	6.4	34
	10 hr	5.20	-	0.53	5.2	46
	12 hr	5.60	-	0.45	3.5	60
	21 hr	6.20	-	0.40	2.2	77
	28 hr	5.8	-	0.34	3.5	61
Plexiglass Reactor, 950 rpm, 100 ml/min O_2						
A7	11 min	4.24	65	1.0	9.8	2
	30 min	4.15	59	0.86	9.1	9
	60 min	4.50	65	0.61	7.4	26
	100 min	4.65	65	0.31	5.2	48
	130 min	4.80	64	0.16	3.9	61
	170 min	4.95	55	0.08	2.9	71

Run No.	Time (min)	pH	T(°C)	1 N H_2SO_4 added (ml)	Total Sulfite (M)	Adipic Acid (mM)	% Degradation
A8-1	0	5	56	0	0.75	9.5	0
	10	5	58	4	0.70	8.6	10
	20	5	60	12	0.58	8.3	13
	30	5	61	20	0.57	8.5	10
	45	5	64	30	0.48	8.3	13
	60	5	65	40	0.38	8.0	16
	80	5	66	53	0.27	7.4	22
	100	5	66	65	0.13	7.0	27
	130	4.8	63	71.3	0.03	4.4	54
A8-2	0	5	55	0	0.79	8.0	0
	10	5	57	0	0.72	7.0	13
	20	5	-	-	0.67	7.0	13
	40	5	61	1.5	0.60	6.7	16
	55	5	63	2.3	0.52	5.3	34

Table 3-16 (continued)

Run No.	Time (min)	pH	T(°C)	1 N H_2SO_4 added (ml)	Total Sulfite (M)	Adipic Acid (mM)	% Degradation
(A8-2)	70	4.9	67	15.6	0.39	3.3	59
	85	4.6	69	28.3	0.26	2.2	72
	105	5	70	28.3	0.11	2.0	75
	130	3.7	66	28.3	0.06	1.7	79
A8-3	0	5	53	0	0.72	9.5	0
	10	5.1	55	2.9	0.65	9.5	0
	20	5	57	11.4	0.58	9.5	0
	30	5	59	20.4	0.52	9.5	0
	45	5	61	33.8	0.44	9.5	0
	60	5	62	44.6	0.34	9.5	0
	80	5	67	55.0	0.25	8.4	12
	100	5	62	66.0	0.18	8.0	16
	133	5	60	76.0	0.08	7.3	23
A9	0	5.1	55	0	0.92	9.7	0
	10	5.2	57	0	0.84	-	-
	27	5.2	60	0	0.71	8.9	8
	40	5.1	61	0	0.59	-	-
	60	5.1	62	0	0.46	8.4	12
	80	5.0	67	0	0.33	-	-
	100	5.0	62	0	0.20	7.6	22
	120	3.0	60	0	0.09	-	-
A10	0	4.3	54	0	0.78	9.4	0
	11	4.3	57	9	0.73	-	-
	20	4.3	60	13	0.63	-	-
	30	4.3	-	15	0.57	7.8	17
	45	4.3	64	19	0.50	-	-
	60	4.3	66	22	0.40	7.8	17
	80	4.3	-	26	0.25	-	-
	100	4.3	68	31	0.15	7.8	17
	120	2.5	67	33	0.14	-	-
				3 N H_2SO_4 added (ml)			
A11	0	6	52	0	0.9	10	0
	60	6	39	0.2	0.9	10	0
	120	6	55	1.9	0.9	10	0
Plexiglass Reactor, 1340 rpm, 130 ml/min O_2							
A12	0	4.3	54	0	-	-	-
	15	4.3	59	0	0.87	10	0
	30	4.3	64	0	0.73	9.1	9
	50	4.3	69	0	0.50	8.8	12
	65	4.3	72	0	0.35	7.1	29

Table 3-16 (continued)

Run No.	Time (min)	pH	T(°C)	3 N H_2SO_4 added (ml)	Total Sulfite (M)	Adipic Acid (mM)	% Degradation
(A12)	80	4.3	73	0	0.18	-	-
	90	4.3	74	0	0.09	6.9	31
A13	0	4.3	52	0	0.95	10.5	0
	35	4.25	67	0.3	0.86	10	5
	85	-	71	0.3	0.06	10	5
A14	0	5.0	52	0	0.95	9.2	0
	35	5.1	54	-	0.90	7.3	5
	95	5.0	55	2	0.83	7.8	16
A15	0	5.0	51	0	0.95	9.9	0
	12	5.0	58	0	0.86	9.1	8
	20	5.0	62	0.6	0.75	8.8	11
	35	5.0	67	0.8	0.57	8.7	12
	60	5.0	73	1.2	0.26	8.9	10
	90	5.0	67	1.3	0.06	8.7	12
A16	0	5.5	55	0	0.97	10.2	0
	10	5.5	59	0	0.86	9.6	6
	20	5.6	63	0.3	0.74	8.6	16
	35	5.4	66	1.1	0.57	8.0	22
	60	5.5	68	1.4	0.30	7.6	25
	90	5.0	65	4.0	0.04	6.6	35
A17	0	4.7	55	0	0.97	10.5	0
	10	4.7	60	0.2	0.88	10.0	4
	20	4.7	-	1.7	0.75	9.9	5
	35	4.7	69	3.0	0.57	9.0	14
	60	4.7	73	3.1	0.27	8.5	19
	85	-	69	-	0.07	8.5	19
	(hr)						
A18	0	5.0	57	0	1.06	9.2	0
	0.5	5.0	56	0.6	1.01	9.2	0
	1.1	5.0	56	3.0	0.95	9.3	0
	2.0	4.9	56	7.4	0.86	8.2	11
	3.0	5.1	56	9.3	0.76	7.0	23
	4.25	5.1	63	11.1	0.37	4.1	55
	5.0	4.1	-	21.7	0.08	2.8	70
				10 N H_2SO_4 added (ml)			
A19	0	5.5	55	0	0.94	8.0	0
	2	5.5	55	1.5	0.86	8.0	0
	3.8	5.5	55	1.8	0.81	7.7	4

Table 3-16 (continued)

Run No.	Time (hr)	pH	T(°C)	10 N H_2SO_4 added (ml)	Total Sulfite (M)	Adipic Acid (mM)	% Degradation
(A19)	4.2	5.5	55	2.0	0.79	7.7	4
	5.2	5.5	56	3.0	0.73	5.8	28
	5.7	5.5	58	3.2	0.60	5.3	34
	6.1	5.5	65	4.0	0.43	4.0	51
	6.4	5.5	72	4.2	0.14	2.0	75
	(min)						
A20	0	5.0	57	0	0.88	8.5	0
	10	5.0	59	0.2	0.84	8.5	0
	25	5.0	63	0.5	0.69	7.0	18
	40	5.0	66	0.7	0.54	5.9	31
	60	5.0	67	1.2	0.36	4.8	44
	90	5.0	67	1.7	0.08	2.6	69
	(hr)						
A21	0	5.0	55	0	0.96	5.6	0
	3	5.0	58	0.9	0.50	2.6	54
	4.5	5.0	60	1.2	0.09	1.4	74
	(min)						
A22	0	5.0	54	0	0.92	11	0
	75	5.0	53	0	0.63	9.2	16
	130	4.9	55	0.5	0.06	6.4	42
A23	0	5.0	55	0	0.90	21.3	0
	35	5.0	68	1.1	0.48	18.7	12
	90	4.6	60	1.7	0.06	17.2	19
A24	0	4.3	52	0	0.90	10	0
	15	4.3	54	0	-	-	-
	34	4.3	57	0	-	-	-
	50	4.3	57	0	0.77	-	-
	75	4.3	60	0	0.63	8.5	15
	100	4.3	68	0	0.43	7.6	24
	110	4.3	72	0	0.28	7.2	28
	120	4.3	74	0	0.17	-	-
	135	4.3	72	0	0.07	6.1	39
A25	0	5.0	56	-	1.1	10.7	0
	20	5.0	59	-	0.82	9.7	9
	40	5.0	64	-	0.69	8.7	19
	60	5.0	69	-	0.47	6.5	39
	80	5.0	73	-	0.22	5.6	47
	100	4.1	69	-	0.05	3.6	66

Table 3-16 (continued)

Run No.	Time (min)	pH	T(°C)	10 N H_2SO_4 added (ml)	Total Sulfite (M)	Adipic Acid (mM)	% Degradation
A26	0	5.5	54	-	0.98	10.3	0
	11	5.5	59	-	0.86	-	-
	20	5.5	62	-	0.78	10.0	3
	35	5.5	69	-	0.59	10.0	3
	60	5.5	71	-	0.25	8.3	20
	75	5.4	76	-	0.04	8.3	20
	90	-	-	-	-	-	-

Table 3-17.

Experimental Data Collected by Y. Lee

Run No.	Time(hr)	pH	T(°C)	$3NH_2SO_4$ added (ml)	Total sulfite (M)	Adipic Acid (mM)	Hydroxyacetic Acid (mM)
AA1	0	5.52	52.0		1.64	9.2	
	1	5.52	65.5		1.29	7.8	
	1.75	5.52	66.8		1.09	6.5	
	2.25	5.52	68.0		0.85	4.8	
	2.75	5.52	72.8	3.70	0.58	4.3	
	3.25	5.52	81.0		0.18	3.7	
AA2	0	5.50	53.0	0	1.67	9.7	11.4
	0.75	5.52	64.0	0.96	1.45	8.6	11.4
	1.50	5.52	67.5	2.05	1.34	8.4	11.8
	2.25	5.52	65.0	3.24	1.18	7.5	11.0
	3.00	5.52	63.0	4.85	0.95	7.0	10.9
	4.25	5.52	74.0	8.54	0.21	4.5	8.4
	4.50	4.40	71.5	8.91	0.07	4.2	8.5
AA3	0	4.50	48.0	0	1.97	9.4	
(10 mM	0.75	4.50	61.6	0.03	1.58	9.3	
glycolic)	1.50	4.50	66.0	0.03	1.23	9.2	
	2.25	4.51	68.0	0.03	0.72	9.0	
	3.00	4.49	68.0	0.53	0.35	8.6	
	3.75	4.53	73.0	0.87	-	8.5	
AA4	0	4.50	45.0	0	1.72	10.7	
(1 mM	1.50	4.51	50.1	0	1.72	10.9	
S_2O_3)	3.00	4.46	53.0	0	1.70	10.8	
AA5	0	4.50	53.0		1.70	10.7	
(1 mM	1.00	4.49	67.6		1.27	10.2	
S_2O_3	2.00	4.48	67.6		0.87	9.7	
1 mM Mn)	3.00	4.42	78.6		0.05	9.4	
	3.50	3.20	68.5		0	9.2	
AA6	0	5.0	51.5	0	0.73	10.0	
(0.3M $MgSO_4$	0.50	4.9	64.2	0.12	0.55	9.8	
1 mM S_2O_3)	1.00	4.7	70.4	0.12	0.19	7.7	
	1.50	4.6	72.2	0.12	0	9.2	
AA7	0	5.0	50.6	0	0.77	9.9	
(0.3M $MgSO_4$	2.00	5.0	53.2	0.55	0.75	9.9	
10 mM S_2O_3)	6.67	4.9	54.0	0.55	0.67	10.1	

Run No.	Time(hr)	pH	T(°C)	$3NH_2SO_4$ added (ml)	Total sulfite (M)	Adipic Acid (mM)
AA8 (0.3M $MgSO_4$ 10 mM S_2O_3 0.3 mM Mn)	0	5.0	54.0	0	0.67	10.1
	0.50	4.7	65.2	0	0.44	9.3
	1.00	3.2	58.0	0	0	9.1
AA9 (10 mM S_2O_3 1 mM Mn)	0	5.5	53.0	0	1.01	10.0
	1.00	5.5	53.0	0	1.00	10.0
AA10 (10 mM S_2O_3 1 mM Mn)	0	5.0	52.0	0	1.00	10.0
	1.00	5.0	52.0	0	1.00	10.0
AA11 (10 mM S_2O_3 1 mM Mn)	0	4.5	51.0	0	0.99	10.0
	1.00	4.5	52.0	0.64	1.05	10.0
	2.00	4.5	52.0	1.08	0.99	10.0
	2.50	4.5	52.0	1.16	1.00	10.0
AA12 (1 mM S_2O_3)	0	5.5	44.0	0	1.04	10.5
	1.00	5.5	51.0	0	0.96	10.0
	2.00	5.5	54.0	0	0.89	10.0
AA13 (1 mM S_2O_3 1 mM Mn)	0	5.5	54.0	0	0.81	10.0
	0.50	5.5	64.0	0	0.64	10.0
	1.25	5.5	73.0	0.13	0.17	8.4
	1.67	5.0	68.0	0.20	0.02	7.1
AA14 (3 mM S_2O_3 1 mM Mn)	0	5.5	49.4		0.94	10.1
	0.50	5.5	51.7		0.94	10.0
	1.50	5.5	52.8		0.94	10.0
	2.50	5.5	52.8		0.94	9.9
AA15 (3 mM S_2O_3 1 mM Mn)	0	5.0	51.7		0.94	9.9
	0.75	5.0	51.7		0.94	9.3
AA16 (3 mM S_2O_3 1 mM Mn)	0	4.5	51.1		0.94	9.3
	0.83	4.5	58.3		0.84	9.0
	2.08	4.1	74.4		0.03	8.4
AA17 (2 mM S_2O_3 1 mM Mn)	0	5.5	45.6		0.98	10.0
	1.00	5.5	51.7		0.97	9.8
	2.67	5.5	53.3		0.97	10.1
	3.50	5.5	53.3		0.96	10.0

Run No.	Time(hr)	pH	T(°C)	3NH$_2$SO$_4$ added(ml)	Total sulfite (M)	Adipic acid(mM)	Glutaric	Succinic
AA18 (2 mM S_2O_3 1 mM Mn)	0	5.0	53.3		0.96	10.0		
	0.50	5.0	62.8		0.69	9.5		
	1.00	5.0	70.0		0.44	9.1		
	1.50	4.9	73.9		0.13	9.3		
	2.00	4.4	66.7		0.05	8.9		
AA19 (1.2 mM S_2O_3 1 mM Mn)	0	5.5	45.6	0	0.95	10.7		
	0.50	5.5	60.6	0.52	0.75	11.0		
	1.00	5.5	67.8	0.52	0.50	9.6		
	1.50	5.5	72.8	0.52	0.4	9.6		
	2.17	5.5	71.1	0.52	0.05	8.8		
	4.00	5.2	55.6	0.52	0	8.8		
AA20 (0.5 mM S_2O_3 1 mM Mn)	0	5.5	51.1	0	0.88	10.3		
	0.58	5.5	62.8	0.23	0.64	10.0		
	0.92	5.5	66.7	0.38	0.47	8.8		
	1.33	5.5	71.7	0.57	0.23	8.4		
	1.67	5.4	73.9	0.64	0.06	8.1		
	3.00	4.8	55.0	0.64	0	8.0		
AA21 (0.1 mM Mn)	0	5.5	55.6	0	1.20	6.8	1.8	0.8
	0.83	5.5	62.8	2.39	0.96	4.6	1.4	0.8
	1.67	5.5	62.2	4.71	0.69	2.8	1.2	0.5
	2.50	5.5	58.3	5.83	0.56	1.8	0.7	0.3
	3.33	5.5	56.1	6.30	0.49	2.0	0.5	0.5
	4.17	5.5	55.0	6.66	0.44	1.4	0.6	0.3
	14.50	5.5	53.3	8.63	0.18	1.4	0.5	0.8
AA22 (3 mM Mn)	0	5.5	52.2	0	0.81	9.8		
	0.33	5.5	59.4	0.45	0.64	10.4		
	0.67	5.5	64.4	1.11	0.51	10.4		
	1.00	5.5	67.2	1.30	0.35	10.0		
	1.33	5.5	68.9	1.66	0.18	10.0		
	1.67	5.5	70.0	1.96	0.03	9.6		
AA23 (3 mM Mn)	0	5.5	56.7	0	0.68	9.1		
	0.33	5.5	62.2	0.24	0.56	8.1		
	0.67	5.5	67.2	0.52	0.40	8.1		
	1.00	5.5	70.0	0.92	0.23	7.2		
	1.33	5.5	71.1	1.29	0.07	5.6		
	1.50	4.9	68.3	1.33	-	5.2		
AA24 (0.1 mM Mn)	0	5.5	46.1	0	1.11			
	0.50	5.5	54.4	0.38	0.96			
	1.00	5.5	61.1	0.98	0.79			
	1.50	5.5	62.2	1.57	0.60			
	2.00	5.5	65.0	2.08	0.45			

Run No.	Time(hr)	pH	T(°C)	$3NH_2SO_4$ added(ml)	Total sulfite (M)	Adipic acid(mM)	
AA24 (cont)	2.50	5.5	63.3	2.58	0.35		
	3.00	5.5	62.2	2.92	0.30		
	3.50	5.5	60.6	3.22	0.22		
	4.17	5.5	58.9	3.57	0.13		
							Glutaric (mM)
G1	0	4.6	55.0		0.82		9.8
	0.16	4.6			0.80		9.7
	0.33	4.6			0.75		9.2
	0.58	4.6			0.66		9.5
	1.00	4.6			0.52		9.0
G2 (1 mM Mn)	0	5.5	46.1	0	0.95		9.7
	0.58	5.5	57.8	0.63	0.74		10.0
	1.00	5.5	60.8	1.16	0.60		9.7
	1.50	5.5	65.6	1.75	0.45		9.0
	2.00	5.5	71.1	2.48	0.14		8.5
	2.67	4.4	55.0	2.51	-		7.5
G3	0	5.5	50.9	0	1.47		9.1
	5.00	5.5	52.8	0.29	1.42		8.0
	13.67	5.5	52.8	1.53	1.37		6.7
	21.33	5.5	52.2	2.31	1.35		6.1
	40.50	5.4	51.7	3.31	1.14		5.6
	63.50	5.3	49.4	4.98	0.99		4.8
	81.67	5.3	50.0	5.58	0.88		1.8
G4 (0.1 mM Mn)	0	5.5	53.9	0	0.88		9.2
	0.50	5.5	61.7	1.15	0.73		7.3
	1.00	5.5	66.1	2.73	0.58		5.9
	1.50	5.5	66.7	3.97	0.41		4.4
	2.00	5.5	65.0	4.66	0.33		3.3
	2.50	5.5	62.2	5.33	0.29		3.1
	3.00	5.5	60.0	5.66	0.24		2.4
	3.75	5.5	58.9	6.07	0.19		1.6
							Succinic (mM)
S1	0	4.5	48.0		1.00		9.5
	0.33	4.5	55.1		0.83		8.4
	0.67	4.5	62.2		0.67		8.1
	1.00	4.5	64.4		0.53		7.4
	1.33	4.5	66.4		0.36		6.9
	1.67	4.5	67.8		0.19		6.9
	2.00	4.5			0.06		5.8
S2 (1 mM Mn)	0	4.4	44.4		1.02		9.3
	0.33	4.5	55.6		0.91		8.4
	0.67	4.5	63.3		0.69		8.8

Run No.	Time(hr)	pH	T(°C)	3NH$_2$SO$_4$ added(ml)	Total sulfite (M)	Adipic acid(mM)	Succinic (mM)
S2 (cont)	1.00	4.5	68.3		0.44		9.2
	1.33	4.5	71.7		0.18		9.2
	1.67	4.0	71.1		0.02		9.8
	1.92	2.9	65.0		0		8.9
S3A	0	5.5	48.0		1.42		10.0
S3B (1 mM Mn)	1.50	5.5	53.0		1.33		6.3
	0	5.5	53.0	0	1.33		6.3
	0.50	5.5	60.5	1.38	1.12		6.6
	1.00	5.5	63.2	4.29	0.92		6.8
	1.50	5.5	64.5	5.35	0.77		6.9
	2.00	5.5	65.6	8.02	0.59		6.7
	2.50	5.5	68.0	10.56	0.34		6.3
	3.00	5.2	72.2	11.62	0.05		6.0
	3.50	4.4	61.5	11.62	0.01		5.9
S4 (0.33 mM Mn)	0	4.5	40.0		0.87		8.4
	0.33	4.5	51.5		0.72		9.5
	0.67	4.5	58.5		0.56		10.2
	1.00	4.4	62.0		0.44		10.3
	1.50	4.4	65.0		0.25		10.2
	2.00	4.4	68.0		0.03		10.0
S5 (0.1 mM Mn)	0	4.4	46.5		1.01		8.7
	0.50	4.4	56.0		0.81		6.1
	1.00	4.5	64.0		0.48		4.9
	1.50	4.4	68.2		0.22		4.7
	1.75	4.3	71.0		0.06		4.6
	2.00	2.5	66.0		0		4.5
S6 (0.2 mM Mn)	0	4.5	38.9	0	1.04		0.84
	0.50	4.5	50.6	0.28	0.89		0.88
	1.00	4.5	58.9	0.82	0.71		0.86
	1.50	4.5	62.2	1.01	0.60		0.82
	2.00	4.5	65.0	1.15	0.45		0.78
	2.83	4.5	69.4	1.39	0.10		0.68
							β-hydroxypropionic (mM)
HP1	0	4.5	53.5	0	0.99		2.1
	0.33	4.5	59.5	3.10	0.87		2.0
	0.67	4.5	64.4	3.50	0.69		2.0
	1.00	4.5	66.6	4.42	0.55		1.9
	1.50	4.5	69.5	4.59	0.27		1.8
	1.75	4.5	71.0	4.62	0.11		1.5
	2.00	2.5	68.4	4.62	-		1.4
	2.50	2.5	60.0	4.62	-		1.3

Run No.	Time(hr)	pH	T(°C)	$3NH_2SO_4$ added(ml)	Total sulfite (M)	Adipic acid(mM)	β-hydroxypropionic (mM)
HP2	0	4.5	48.9	0	0.93		11.8
	0.50	4.5	59.7	2.74	0.74		10.5
	1.00	4.5	64.4	2.74	0.49		10.4
	1.50	4.4	67.8	2.74	0.25		10.2
	1.75	4.3	68.9	2.74	0.12		10.2
HP3	0	4.5	45.0		0.97		24.3
	0.33	4.5	47.6		0.92		25.7
	0.67	4.5	49.2		0.85		25.7
	1.00	4.5	50.5		0.83		25.7
	1.50	4.5	51.6		0.88		26.0
	2.00	4.5	51.6		0.85		26.0
HP4 (1.0 mM Mn)	0	5.5	52.0	0	0.83		25.9
	0.33	5.5	57.5	0.89	0.70		22.6
	0.67	5.5	64.2	4.82	0.55		22.1
	1.00	5.5	70.0	8.05	0.29		22.3
	1.42	5.0	72.0	8.58	0.03		22.0
HP5	0	4.5	42.0	0	0.97		9.8
	0.50	4.5	48.0	0.25	0.95		10.2
	1.00	4.5	50.0	5.76	0.90		10.3
	1.67	4.4	52.5	8.03	0.89		10.3
	2.42	4.4	55.0	11.53	0.78		10.1
	3.17	4.4	56.5		0.68		9.6
							Glycolic
HA1	0	4.5	49.0		1.00		8.3
	0.50	4.5	52.0		0.96		8.4
	1.00	4.5	53.0		0.94		8.9
	1.75	4.5	54.0		0.92		9.1
	2.50	4.5	54.0		0.88		8.6
	3.25	4.5	54.0		0.84		8.6
	4.00	4.5	54.0		0.82		8.6
							Hydroxyacetic (mM)
HA2 (1 mM Mn)	0	5.5	43.0	0	0.80		9.9
	0.33	5.5	50.0	0.31	0.74		10.3
	0.67	5.5	55.0	0.48	0.64		10.1
	1.00	5.5	59.0	0.48	0.55		10.8
	1.33	5.4	65.0	0.85	0.30		10.6
	1.67	5.1	70.0	1.11	0.07		10.7
HA3	0	5.0	38.0		1.01		9.6
	2.00	5.0	53.0		1.02		9.9
	4.00	5.0	53.5		0.97		9.7
	6.00	5.0	53.5		0.95		10.2

Run No.	Time(hr)	pH	T(°C)	$3NH_2SO_4$ added(ml)	Total sulfite (M)	Adipic acid(mM)	Hydroxyacetic (mM)
HA3 (cont)	8.00	5.0	53.5		0.91		10.0
HA4 (0.1 mM Mn)	0	5.0	45.0		0.94		10.1
	1.00	5.0	52.5		0.89		9.8
	2.00	5.0	54.0		0.84		9.9
	2.50	5.0	55.0		0.80		10.0
	3.50	5.0	55.5		0.75		9.5
	4.50	5.0	55.5		0.69		9.9
HA5 (0.3 mM Mn)	0	5.0	48.0	0	0.96		8.1
	0.50	5.0	56.2	2.37	0.82		8.0
	1.08	5.0	63.5	2.61	0.59		7.9
	1.50	5.0	65.8	2.61	0.45		7.6
	1.78	4.9	67.2	2.61	0.32		7.4

Run No.	Time(hr)	pH	T(°C)	$3NH_2SO_4$ added(ml)	Total sulfite (M)	Adipic acid(mM)	Glutaric	Succinic
M1 (1 mM Mn)	0	5.5	49.4	0	1.36	1.1	5.2	0.6
	0.50	5.5	46.7	0.21	1.22	1.0	5.1	0.8
	1.00	5.5	60.0	0.48	1.10	1.0	5.0	0.9
	1.50	5.5	60.6	0.73	1.00	1.0	4.9	1.1
	2.00	5.5	61.0	1.09	0.85	1.0	5.0	1.4
	2.50	5.5	61.1	1.32	0.75	0.9	4.6	1.5
	3.50	5.5	67.8	2.14	0.42	0.8	4.2	2.0
	4.67	4.9	64.4	2.73	-	0.6	3.2	2.8
M2 (1 mM S_2O_3 1 mM Mn)	0	5.5	50.6	0	0.92	2.7	11.4	5.4
	0.50	5.5	64.4	0.86	0.73	2.7	11.4	5.8
	1.00	5.5	70.6	1.66	0.44	2.7	11.4	6.2
	1.67	5.5	73.3	2.42	0.07	2.7	11.2	6.6
	2.00	5.2	64.4	2.42	-	2.4	10.0	7.1
M3	0	4.0	50.0	0	0.94	2.9	11.4	5.4
	0.50	4.0	62.8	0	0.68	2.8	11.2	5.5
	1.00	3.9	67.8	0	0.43	2.7	10.8	5.5
	1.50	3.7	71.1	0	0.14	2.7	10.5	5.5
	1.83	2.0	66.1	0	-	2.5	10.5	5.2

Run No.	Time(hr)	pH	T(°C)	$3NH_2SO_4$ added(ml)	Total sulfite (M)	Adipic acid(mM)	Glutaric	Succinic	% Degradation
M4	0	5.0	53.9	0	1.06	2.4	10.5	5.2	0
	0.50	5.0	57.2	1.08	0.98	2.4	11.0	5.0	0
	1.00	5.0	58.9	1.74	0.90	2.1	9.7	4.5	10
	1.50	5.0	58.9	2.40	0.77	2.0	9.0	4.4	15
	2.00	5.0	58.9	3.08	0.67	2.0	9.2	4.4	14
	2.50	5.0	58.3	3.57	0.60	1.8	8.4	4.0	22
	3.17	5.0	57.8	4.37	0.50	1.6	7.8	3.6	23
	4.67	5.0	56.7	5.78	0.40	1.6	6.9	3.5	34

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Run No.	Time(hr)	pH	T(°C)	$3NH_2SO_4$ added(ml)	Total sulfite (M)	Adipic acid(mM)	Glutaric	Succinic	% Degradation
M4	6.83	5.0	55.6	7.57	0.21	1.2	6.0	3.2	43
(cont)	9.00	4.8	54.4	9.03	-	0.6	4.0	2.2	62
						Fumaric		**% Degradation**	
F1	0	5.5	51.0	0	1.43	6.8		0	
(1 mM	0.50	5.5	58.8	1.77	1.11	5.6		18	
Mn)	1.08	5.5	61.9	3.01	0.98	4.1		40	
	1.50	5.5	63.0	3.61	0.91	3.0		56	
	2.00	5.5	63.9	4.20	0.78	2.4		65	
	3.00	5.5	65.8	5.04	0.47	1.5		78	
	4.00	4.4	68.0	5.31	0.02	1.8		74	

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SECTION 3

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